

Message

**From:** Richard, Ann [/O=EXCHANGELABS/OU=EXCHANGE ADMINISTRATIVE GROUP (FYDIBOHF23SPDLT)/CN=RECIPIENTS/CN=8980B96D55AE4A268DB3CD9BC3E5A865-RICHARD, ANN]  
**Sent:** 2/23/2021 8:04:29 PM  
**To:** Lesley Hay Wilson [lhay\_wilson@sagerisk.com]  
**Subject:** RE: ITRC PFAS Documents  
**Attachments:** PFAS\_Section2(11-18-20) ar.docx

Sorry about that, Lesley. I blame the late hour. I'm attaching the Word doc version of that pdf where I tracked my changes. Sorry if it's not in the ideal format, but am hoping you can transfer whatever edits you approve to the correct document.

Thanks!

Ann M Richard, PhD  
Research Chemist  
Mail Drop D143-02  
Center for Computational Toxicology & Exposure (CCTE)  
Computational Chemistry & Cheminformatics Branch  
Office of Research & Development  
US Environmental Protection Agency  
Research Triangle Park, NC 27711  
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office: EPA Main Facility, Rm D131C

**From:** Lesley Hay Wilson <lhay\_wilson@sagerisk.com>  
**Sent:** Tuesday, February 23, 2021 1:34 PM  
**To:** Richard, Ann <Richard.Ann@epa.gov>  
**Subject:** Re: ITRC PFAS Documents

Ann –  
The file, PFAS\_Section2(11-18-20) ar.pdf, I received only has a highlight on lines 95 - 96 the sentence about compounds with an aromatic component. Is this the correct file? I've attached the Word version of the file if you can paste your edits in there. We were also hoping that you could briefly expand the sentence about CompTox that appears at lines 98 and 99.

Thank you for your help,  
Lesley

\*\*\*\*\*

Lesley Hay Wilson, Ph.D.  
Sage Risk Solutions LLC  
[lhay\\_wilson@sagerisk.com](mailto:lhay_wilson@sagerisk.com)  
phone: 512-327-0902

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I have attached to this email the text of the team review post, the Team Review 2 version of Section 2, and the blank comments collector spreadsheet. If you have comments on Section 2, you can provide them in the comments spreadsheet.

As we discussed, for early next week it would be great to get a paragraph that describes the EPA comptox database and some of the information available to users.

Let me know if you have questions,

Lesley

\*\*\*\*\*

Lesley Hay Wilson, Ph.D.  
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## 1. Introduction

15 Per- and polyfluoroalkyl substances (PFAS) ~~are constitute a very large family of fluorinated thousands~~  
of chemicals, exceeding several thousand in commercial use or the environment,

16 that vary widely in their chemical and physical properties, as well as their potential risks to  
17 human health and the environment.

18 An early and widely recognized technical definition of PFAS ~~is was~~ provided by Buck et al. (2011)  
19 who defined PFAS as, “highly fluorinated aliphatic substances that contain one or more carbon  
20 (C) atoms on which all the hydrogen (H) substituents (present in the nonfluorinated analogues  
21 from which they are notionally derived) have been replaced by fluorine (F) atoms, in such a  
22 manner that they contain the perfluoroalkyl moiety  $C_nF_{2n+1}-$ .”

Buck et al. (2011) provides a definition of PFAS (see text

23 box) stating that all PFAS contain within their molecular structure a straight or branching chain  
24 of carbon atoms in which one or more of the carbon atoms have fluorine atoms attached at all  
25 bonding sites not occupied by another carbon atom and the fluorinated part of the molecule (the

26 “perfluoroalkyl moiety”) can be expressed as  $C_nF_{2n+1}-$ . This definition has expanded as the scope of  
chemicals being considered under the umbrella of PFAS chemistry has broadened considerably over the  
past decade to include both polyfluorinated substances (i.e., where the alkyl chain is not fully  
fluorinated) and polymers.

27 Fundamentally ~~Broadly speaking~~, PFAS are characterized by ~~as having~~ carbon atoms that are linked  
together bonded with to fluorine

28 atoms attached to the carbons whereby fluorination imparts unique properties to the whole  
molecule. Additional ~~Modifying~~ qualifying characteristics, such as addition of a functional group, other  
halogen substitutions (e.g., chlorine), partial fluorination, etc.)

29 are described in Section 2.2 along with evolving definitions of PFAS.

30 <Note: The text box on this page will be deleted. The Buck et al. (2011) quoted definition is  
31 included in Section 2.2, along with more detailed discussions.>

32

## 2. PFAS Chemistry and Naming Conventions, History and Use of PFAS, and Sources of

### PFAS Releases to the Environment

33 PFAS chemistry was discovered in the late 1930s. The first perfluorinated chemical to be discovered in  
the late 1930's by a DuPont researcher was the polymer, Polyfluoroethylene, or PFTE. A decade later,

Commented [AMR1]: [https://en.wikipedia.org/wiki/Time\\_line\\_of\\_events\\_related\\_to\\_per-\\_and\\_polyfluoroalkyl\\_substances#cite\\_note-NYT\\_Plunkett\\_Obit\\_19940515-16](https://en.wikipedia.org/wiki/Time_line_of_events_related_to_per-_and_polyfluoroalkyl_substances#cite_note-NYT_Plunkett_Obit_19940515-16)



the chemical would be the first PFAS chemical to be used in the commercial production of Teflon. Since the 1950s, many products commonly

used by consumers and industry have been manufactured with or from PFAS, as the unique physical and chemical properties of PFAS impart oil, water, stain, and soil repellency, chemical and thermal stability, and friction reduction to a range of products. These products have application in many industries, including the aerospace, semiconductor, medical, automotive, construction, electronics, and aviation industries, as well as in consumer products (such as carpets, clothing, furniture, outdoor equipment, food packaging), and firefighting applications (3M Company 1999a; Buck et al. 2011; KEMI 2015a; USEPA 2017b).

The number of PFAS and their uses have expanded over the years. ~~It has been estimated that the PFAS family may include approximately 5,000–10,000 chemicals (USEPA 2018).~~ A recent inventory of PFAS identified ~~Chemical Abstracts Service (CAS) Registry Numbers found listed more than 4,700 PFAS with Chemical Abstracts Service (CAS) Registry Numbers that could have been, or may be, on the global market (OECD 2018), although~~ the uses of each of these PFAS may not be known (KEMI 2015a). Publicly available health and toxicity studies are limited to only a small fraction of these PFAS, and modern commercially available analytical technologies typically identify only about 20–30 PFAS.

## 2.2 Chemistry, Terminology, and Acronyms

This section focuses on chemistry, terminology, names, and acronyms for those PFAS most commonly reported in the environment, identified in scientific literature, and those PFAS most commonly tested for by current analytical methods. Other important classes of PFAS are introduced. This section also introduces the chemical manufacturing processes that influence the types of PFAS that are found in the environment.

69

PFAS are characterized by carbon atoms that are ~~linked together with~~ bonded to fluorine atoms attached to the carbons at most or all of the available carbon bonding sites. A more specific and technical definition of PFAS states that PFAS are defined as

~~An early and widely recognized technical definition of PFAS is provided by Buck et al. (2011)~~

**Commented [AMR2]:** clunky wording, prefer simpler bonding

who define PFAS as, "highly fluorinated aliphatic substances that contain one or more carbon (C) atoms on which all the hydrogen (H) substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by fluorine (F) atoms, in such a manner that they contain the perfluoroalkyl moiety  $C_nF_{2n+1}$ ."

**Commented [AMR3]:** no need to repeat here – moved edited text to intro

The definition of PFAS may be evolving to reflect continued study of these compounds and takes different forms depending on the operational criteria used and the intended scope and application of the retrieved dataset. For example, the definition of PFAS used in one study (OECD 2018) expanded the Buck et al. definition to also include chemicals that contain –

$C_nF_{2n}$  – in addition to the  $C_nF_{2n+1}$  –, which includes encompasses chemicals with both ends of the carbon fluorine chain connected to a hydrogen or functional group, such as well as cyclic analogs of linear PFAS.

The U.S. EPA's CompTox Chemicals Dashboard provides a large publicly available resource for PFAS chemicals, structures and predicted properties, and has expanded beyond coverage of the full OECD list cited above. This effort has taken two approaches to defining PFAS chemicals. The first, denoted PFASMASTER ([HYPERLINK "https://comptox.epa.gov/dashboard/chemical\_lists/PFASMASTER"]), was based on a simple join, or combination of publicly available lists of PFAS chemicals reported by other entities, such as the OECD 2018 report. The second approach applied a small set of structure filters to the entire EPA DSSTox database (currently exceeding 900K substances), resulting in a list containing more than 8000 PFAS structures (PFASSTRUC, [HYPERLINK "https://comptox.epa.gov/dashboard/chemical\_lists/PFASSTRUC"]). The PFASMASTER file currently exceeds 9200 substances and includes both PFAS structures (from PFASSTRUC) and structures and non-structurable chemicals (such as mixtures and polymers) from the join of several public PFAS lists. Hence, the structure-based filters used in this effort expand the PFAS definition beyond the Buck et al (2011) and OECD (2018) definitions and are designed to fully encompass publicly available PFAS lists, as well as to be inclusive of small fluorinated chemicals of potential concern to EPA regulators.

**Commented [AMR4]:** [HYPERLINK "https://comptox.epa.gov/dashboard/"] Williams, A.J., Grulke, C.M., Edwards, J. et al. The CompTox Chemistry Dashboard: a community data resource for environmental chemistry. *J Cheminform* 9, 61 (2017). <https://doi.org/10.1186/s13321-017-0247-6>

Whereas PFAS definitions such as provided by EPA's CompTox Dashboard are designed to be broadly inclusive, regulatory applications often must be more circumscribed and precisely worded.

More recently, for example, the Michigan PFAS Action Response Team (MPART) offers a working description/definition of perfluoroalkyl substances, stating that the basic chemical structure is a chain (or tail) of two or more adjacent carbon atoms with a charged functional group head attached at one end. The functional groups commonly are carboxylates or sulfonates, but other forms are also detected in the environment. For a linear or branched aliphatic tail, this structure can be written as:  $C_nF_{2n+1}-R$  where " $C_nF_{2n+1}$ " defines the length of the perfluoroalkyl chain tail, " $n$ " is  $\geq 2$ , and " $R$ " represents the attached functional group head. The tail may be linear, or branched, or contain a cyclic portion, but it always contains adjacent fluorinated carbon atoms in a  $C_nF_{2n+1}$  moiety (with  $n \geq 2$ ). The functional group may contain one or more carbon atoms, which are included in the total number of carbons when naming the compound. Section 2.2.4 of this document provides additional descriptions of perfluoroalkyl substances.

An emerging subject of discussion is whether the presence of an aromatic component in a chemical's structure still constitutes classification as PFAS. Arguments for such inclusion include cases where a perfluoro compound could result from reaction or biotransformation.

For practical reference, the USEPA CompTox chemical dashboard provides useful information about PFAS ([http://comptox.epa.gov/dashboard/chemical\\_lists/PFASMASTER](http://comptox.epa.gov/dashboard/chemical_lists/PFASMASTER)).

[https://comptox.epa.gov/dashboard/chemical\\_lists/PFASMASTER](https://comptox.epa.gov/dashboard/chemical_lists/PFASMASTER)

[https://comptox.epa.gov/dashboard/chemical\\_lists/PFASMASTER](https://comptox.epa.gov/dashboard/chemical_lists/PFASMASTER)

Ann

Ann M Richard, PhD

Research Chemist

Mail Drop D143-02

Center for Computational Toxicology &amp; Exposure (CCTE)

Computational Chemistry &amp; Cheminformatics Branch

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Research Triangle Park, NC 27711

tel: 919-541-3934

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.....

[illegible]

**Subject:** Re: ITRC PFAS Team - History, Use and Naming Conventions writing subgroup

Thank you for looking into the materials. It can be a bit confusing to get oriented with all the work we are doing at ITRC. The Naming Conventions topic of the writing subgroup is definitely the place that we would appreciate your input, review, and comments. We have some new content coming up to Section 2.2 Chemistry, Terminology, and Acronyms of the Tech Reg document <https://pfas-1.itrcweb.org/2-2-chemistry-terminology-and-acronyms/>

I think one topic where we could use a short paragraph that maybe you could write is a description of what information about PFAS users can access through EPA's CompTox database.

\*\*\*\*\*

**Statement of Confidentiality:**

**Subject:** RE: ITRC PFAS Team - History, Use and Naming Conventions writing subgroup

Thanks for the additional info. I confess to being a little confused about what team meeting/subgroup I was being asked to participate in, so apologies for missing the morning call that answered my more general question. I'll review the slides you sent. I also viewed the ITRC YouTube video by Sandra Goodrow on PFAS naming conventions and Phys-Chem Properties and thought it well put together. I'm still not quite sure what role I'm being asked to play, but am happy to play an advisory role for now. Looking at the PFAS Team Subgroups, I suspect that "History, Use, Naming Conventions"

Many thanks,  
Ann

**From:** Lesley Hay Wilson <[lhay\\_wilson@sagerisk.com](mailto:lhay_wilson@sagerisk.com)>  
**Sent:** Wednesday, February 10, 2021 4:55 PM  
**To:** Richard, Ann <[Richard.Ann@epa.gov](mailto:Richard.Ann@epa.gov)>  
**Cc:** Schlosser, KateEmma <[KateEmma.A.Schlosser@des.nh.gov](mailto:KateEmma.A.Schlosser@des.nh.gov)>; [Sandra.Goodrow@dep.nj.gov](mailto:Sandra.Goodrow@dep.nj.gov)  
**Subject:** Re: ITRC PFAS Team - History, Use and Naming Conventions writing subgroup

Thanks for attending the training subgroup call today. I know there is a lot of information to get oriented to ITRC and specifically to the PFAS Team. I am the Program Advisor for the team. I am contracted by ITRC to support the work of the team. On the call today Sandra Goodrow, from NJDEP gave a brief introduction about ITRC. Sandra is one of the PFAS Team Leaders; our other Team Leader is Kate Emma Schlosser from NH DES. All of the members of the team volunteer their time to work on the team.

The Interstate Technology and Regulatory Council (ITRC) is a state-led coalition working to reduce barriers to the use of innovative environmental technologies and approaches so that compliance costs are reduced and cleanup efficacy is maximized. ITRC produces documents and training that broaden and deepen technical knowledge and expedite quality regulatory decision making while protecting human health and the environment. With private and public sector members from all 50 states and the District of Columbia, ITRC truly provides a national perspective. More information on ITRC is available at [www.itrcweb.org](http://www.itrcweb.org). ITRC is a program of the Environmental Research Institute of the States (ERIS), a 501(c)(3) organization incorporated in the District of Columbia and managed by the Environmental Council of the States (ECOS). ECOS is the national, nonprofit, nonpartisan association representing the state and territorial environmental commissioners. Its mission is to serve as a champion for states; to provide a clearinghouse of information for state environmental commissioners; to promote coordination in environmental management; and to articulate state positions on environmental issues to Congress, federal agencies, and the public.

We held a new members call this morning. I have attached the slides from that call that include background information about the team and how to access information on the PFAS Team private page  
<https://www.itrcweb.org/Team/Private?teamID=78>

The PFAS team has members from state environmental agencies, City/Local governments, consulting & industry, federal partners – USEPA, DOE and DOD, stakeholders, academics and some international members.

Please contact Kate Emma, Sandra or me if you have any questions.

Regards,  
Lesley

\*\*\*\*\*

Lesley Hay Wilson, Ph.D.  
Sage Risk Solutions LLC  
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phone: 512-327-0902

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**From:** Lesley Hay Wilson <[lhay\\_wilson@sagerisk.com](mailto:lhay_wilson@sagerisk.com)>

**Date:** Tuesday, January 26, 2021 at 3:23 PM

**To:** <[Richard.Ann@epa.gov](mailto:Richard.Ann@epa.gov)>

**Cc:** "Schlosser, KateEmma" <[KateEmma.A.Schlosser@des.nh.gov](mailto:KateEmma.A.Schlosser@des.nh.gov)>, "Goodrow, Sandra" <[Sandra.Goodrow@dep.nj.gov](mailto:Sandra.Goodrow@dep.nj.gov)>, "Hale, Jeffrey" <[Jeffrey.Hale@parsons.com](mailto:Jeffrey.Hale@parsons.com)>, "Wenzel, Jeff" <[Jeff.Wenzel@health.mo.gov](mailto:Jeff.Wenzel@health.mo.gov)>

**Subject:** ITRC PFAS Team - History, Use and Naming Conventions writing subgroup

Hi Ann –

Thank you for joining the ITRC PFAS team. Your expertise in chemical database/modeling/cheminformatics with regard to PFAS, and research in creating structure-based tools and approaches for categorizing PFAS will be a great asset, in particular for the work of the PFAS Team writing subgroup for History, Use and Naming Conventions (Section 2 of the guidance document <https://pfas-1.itrcweb.org/2-pfas-chemistry-and-naming-conventions-history-and-use-of-pfas-and-sources-of-pfas-releases-to-the-environment-overview/>). I am copying the writing subgroup leaders Jeff Hale and Jeff Wenzel so they can give you an overview of the updates that we are working on.

Let us know if you have questions,

Lesley

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Lesley Hay Wilson, Ph.D.  
Sage Risk Solutions LLC  
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Message

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**From:** Lesley Hay Wilson [lhay\_wilson@sagerisk.com]  
**Sent:** 2/19/2021 5:23:08 PM  
**To:** Richard, Ann [Richard.Ann@epa.gov]  
**CC:** Sandra.Goodrow@dep.nj.gov; Schlosser, KateEmma [KateEmma.A.Schlosser@des.nh.gov]  
**Subject:** ITRC PFAS Documents  
**Attachments:** PFAS\_Section2(11-18-20).pdf; Copy of Copy of PFAS\_ExtRev1\_CommentsCombined(1-22-21)\_JW\_JH.xlsx; ITRC PFAS Team forum post(2-13-21).pdf; PFAS\_Section2\_Rev2(2-12-21).pdf; TeamReview2\_PFAS\_CommentSpreadsheet(2-12-21).xlsx

Ann –

Thank you for being on the call today. It was so helpful to have your input. I have attached the document we were reviewing this morning that has the first set of proposed changes, External Review 1, and the comments response spreadsheet that Jeff Hale and Jeff Wenzel are working on.

On the team private page I posted the second set of new content for team review. You should have received an email from the PFAS team email forum last Saturday about External Review 2. The files for that review are on document Drafts > Team Review 2 folder. You start at the team private page:

<https://www.itrcweb.org/Team/Private?teamID=78>

The Document Drafts folder is in the middle, 6 folders down – its Blue, when you click on the bar that says Document Drafts it opens. The Team Review 2 folder is the last one.

I have attached to this email the text of the team review post, the Team Review 2 version of Section 2, and the blank comments collector spreadsheet. If you have comments on Section 2, you can provide them in the comments spreadsheet.

As we discussed, for early next week it would be great to get a paragraph that describes the EPA comptox database and some of the information available to users.

Let me know if you have questions,

Lesley

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## Section 2. Naming Conventions and Use

Review Note: This file contains new content for Sections 1 and 2 of the PFAS Guidance Document (PFAS-1):

- Revision in Section 1 - Introduction
- New text and figure for the main introduction to Section 2.
- Additions in Section 2.2 Chemistry, Terminology and Acronyms
- Additions in Section 2.2.2 Introduction to the PFAS Family
- Revisions in 2.2.3.5 Other Perfluoroalkyl Substances
- Revisions in 2.3.2 Analytical Developments

Please use the comments spreadsheet PFAS\_ExtRev1\_CommentSpreadsheet(11-18-2020).xlsx to provide your comments. Instructions are included in the spreadsheet. If additional context for the change is needed, please refer to the web version of the PFAS Technical and Regulatory Guidance Document, <https://pfas-1.itrcweb.org>.

### 1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a very large family of thousands of chemicals that vary widely in their chemical and physical properties, as well as their potential risks to human health and the environment. Buck et al. (2011) provides a definition of PFAS (see text box) stating that all PFAS contain within their molecular structure a straight or branching chain of carbon atoms in which one or more of the carbon atoms have fluorine atoms attached at all bonding sites not occupied by another carbon atom and the fluorinated part of the molecule (the “perfluoroalkyl moiety”) can be expressed as  $C_nF_{2n+1}$ .

Fundamentally, PFAS are characterized by carbon atoms that are linked together with fluorine atoms attached to the carbons. Additional qualifying characteristics, such as a functional group, are described in Section 2.2 along with evolving definitions of PFAS.

<Note: The text box on this page will be deleted. The Buck et al. (2011) quoted definition is included in Section 2.2, along with more detailed discussions.>

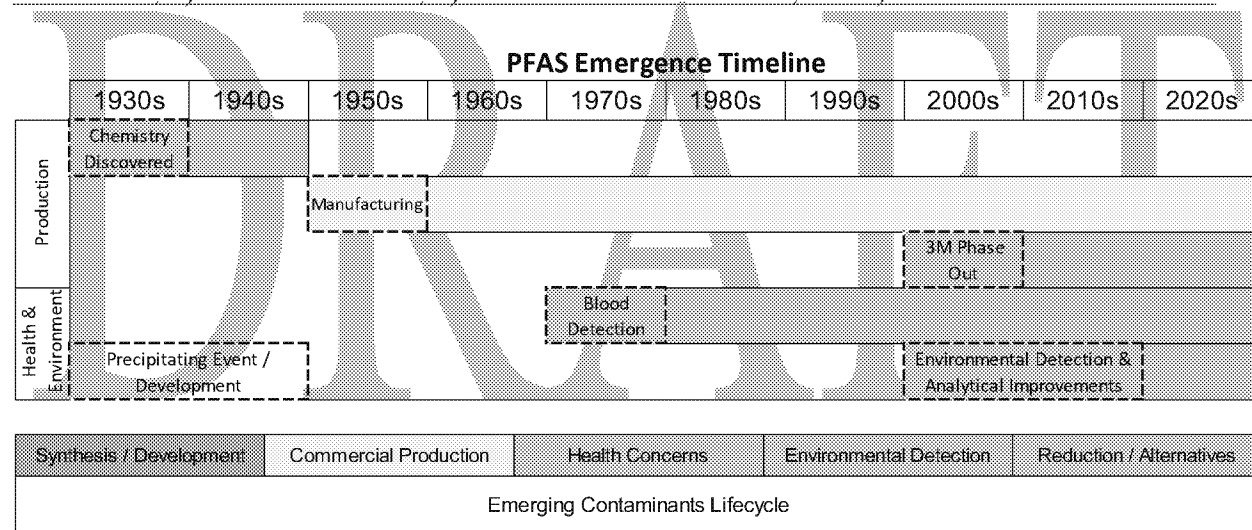
### 2. PFAS Chemistry and Naming Conventions, History and Use of PFAS, and Sources of PFAS Releases to the Environment

PFAS chemistry was discovered in the late 1930s. Since the 1950s, many products commonly used by consumers and industry have been manufactured with or from PFAS, as the unique physical and chemical properties of PFAS impart oil, water, stain, and soil repellency, chemical and thermal stability, and friction reduction to a range of products. These products have application in many industries, including the aerospace, semiconductor, medical, automotive, construction, electronics, and aviation industries, as well as in consumer products (such as carpets, clothing, furniture, outdoor equipment, food packaging), and firefighting applications (3M Company 1999a; Buck et al. 2011; KEMI 2015a; USEPA 2017b).

The number of PFAS and their uses have expanded over the years. It has been estimated that the PFAS family may include approximately 5,000–10,000 chemicals (USEPA 2018i). A recent inventory of PFAS identified Chemical Abstracts Service (CAS) Registry Numbers found more than 4,700 PFAS that could have been, or may be, on the global market (OECD 2018), although the uses of each of these PFAS may not be known (KEMI 2015a). Publicly available health and toxicity studies are limited to only a small fraction of these PFAS, and modern commercially available analytical technologies typically identify only about 20–30 PFAS.

Scientific, regulatory, and public concerns have emerged about potential health and environmental impacts associated with chemical production, product manufacture and use, and disposal of PFAS-containing wastes. These concerns have led to efforts to reduce the use of or replace certain PFAS, such as the two most widely produced, commonly encountered, and most studied compounds: perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (USEPA 2016e; WA DER 2017).

PFAS have followed a similar pattern of emergence and awareness exhibited by many other anthropogenic environmental contaminants. Figure 2-1 provides a general timeline of PFAS emergence and awareness that includes categories of 1) Synthesis/Development, 2) Commercial Production, 3) Health Concerns, 4) Environmental Detection, and 5) Reduction / Alternatives.



**Figure 2-1. General timeline of PFAS emergence and awareness.**

*Graphic is intended to provide a general sense of PFAS emergence and awareness by decade with initial activity or precipitating event indicated for the start of each phase of emergence. It is not intended to be exhaustive or precise.*

*Source: J. Hale, Parsons. Used with permission.*

## 2.2 Chemistry, Terminology, and Acronyms

This section focuses on chemistry, terminology, names, and acronyms for those PFAS most commonly reported in the environment, identified in scientific literature, and those PFAS most commonly tested for by current analytical methods. Other important classes of PFAS are

introduced. This section also introduces the chemical manufacturing processes that influence the types of PFAS that are found in the environment.

PFAS are characterized by carbon atoms that are linked together with fluorine atoms attached to the carbons. A more specific and technical definition of PFAS states that PFAS are defined as An early and widely recognized technical definition of PFAS is provided by Buck et al. (2011) who define PFAS as, “highly fluorinated aliphatic substances that contain one or more carbon (C) atoms on which all the hydrogen (H) substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by fluorine (F) atoms, in such a manner that they contain the perfluoroalkyl moiety  $C_nF_{2n+1}$  -.”

The definition of PFAS may evolve to reflect continued study of these compounds. For example, the definition of PFAS used in one study (OECD 2018) also included chemicals that contain –  $C_nF_{2n}$  – in addition to the  $C_nF_{2n+1}$  -, which includes chemicals with both ends of the carbon-fluorine chain connected to a functional group, such as cyclic analogs of linear PFAS.

More recently, the Michigan PFAS Action Response Team (MPART) offers a working description of perfluoroalkyl substances, stating that the basic chemical structure is a chain (or tail) of two or more adjacent carbon atoms with a charged functional group head attached at one end. The functional groups commonly are carboxylates or sulfonates, but other forms are also detected in the environment. For a linear or branched aliphatic tail, this structure can be written as:  $C_nF_{2n+1}$ -R where “ $C_nF_{2n+1}$ ” defines the length of the perfluoroalkyl chain tail, “n” is  $\geq 2$ , and “R” represents the attached functional group head. The tail may be linear, or branched, or contain a cyclic portion, but it always contains adjacent fluorinated carbon atoms in a  $C_nF_{2n+1}$  moiety (with  $n \geq 2$ ). The functional group may contain one or more carbon atoms, which are included in the total number of carbons when naming the compound. Section 2.2.4 of this document describes polyfluoroalkyl substances.

An emerging subject of discussion is whether the presence of an aromatic component in a chemical’s structure still constitutes classification as PFAS.

For practical reference, the USEPA CompTox chemical dashboard provides useful information about PFAS ([https://comptox.epa.gov/dashboard/chemical\\_lists/PFASMASTER](https://comptox.epa.gov/dashboard/chemical_lists/PFASMASTER)).

## 2.2.2 Introduction to the PFAS Family

PFAS encompass a wide universe of substances with very different physical and chemical properties (Section 4). ~~including gases (for example, perfluorobutane), liquids (for example, fluorotelomer alcohols), and solid material high molecular weight polymers (for example, PTFE). For this reason, it is helpful to group PFAS that share similar chemical and physical properties.~~

As shown in Figure 2-2, the PFAS family may be divided into two primary classes: polymers and nonpolymers. Each class may contain many subclasses, groups, and subgroups, some of which are shown in the figure. This document focuses primarily on those nonpolymer PFAS most commonly detected in the environment and those PFAS that may be significant as “precursors” that can transform to more persistent forms.

**Figure 2-2. The PFAS family.**

The family tree is further expanded in Figure 2-3, based on nomenclature provided in Buck et al (2011), Organization For Economic Co-operation and Development (OECD, 2015b), and Wang, DeWitt, et al (2017), with further introduction to some of these chemicals provided later in this section.

Future updates to the family tree and nomenclature are expected to be necessary given the evolving public knowledge of these compounds. For example, other PFAS without analytical standards are being identified using nontarget analyses by research laboratories (Section 11). These PFAS do not necessarily have an associated CAS number but are being identified by molecular structure.

Figure 2-3 is not inclusive of all PFAS and is intended to categorize a sampling of common PFAS chemistries. Additionally, as more information becomes available, it is likely that there will be changes, until that time, Figure 2-3 and is based on the information included in the references above.

An example of evolving classification includes whether perfluoropolyethers (PFPE) should be regarded as polymers or nonpolymers, since this chemical group can function (or be used) as either a polymer or a nonpolymer depending on the chemical structure (ionic character) and their intended use. These chemicals are often referred to as “Functionalized PFPE.” It is recommended this chemical category be carefully evaluated and not assume that all of the PFPE chemistries will fall into either the polymer or nonpolymer classification.

Functionalized PFPE as a polymer, or Polymeric PFPE, can be used as a grease, solvent or lubricant. They are very large molecules (high molecular weight) and thereby tend to not be bioavailable and stable (not mobile) in the environment. They may have end groups that are significantly smaller, as compared to the length of the repeating units (backbone) and have little to no polar effect (not polarized). Section 2.2.2.1 includes more information about polymer PFAS.

Functionalized PFPE as a nonpolymer, can be used as a surfactant, soap or de-greaser. They are small (low molecular weight) making them more available for bioaccumulation and mobility in the environment. These chemistries have ionic end-groups (heads) which are used to capture or link together like-particles. Examples of Functionalized PFPE nonpolymers are ADONA (Section 2.2.4.3) and GenX (Section 2.2.3.5). Buck et al. (2011), pages 532-533, provides more information about PFPE.

**2.2.3.5 Other Perfluoroalkyl Substances**

Other perfluoroalkyl substances shown on Figure 2-3 include:

- perfluoroalkane sulfonyl fluorides [PASFs, such as perfluorooctane sulfonyl fluoride (POSF) and perfluorobutane
- sulfonyl fluoride (PBSF)], and perfluoroalkanoyl fluorides (PAFs), associated with the ECF process

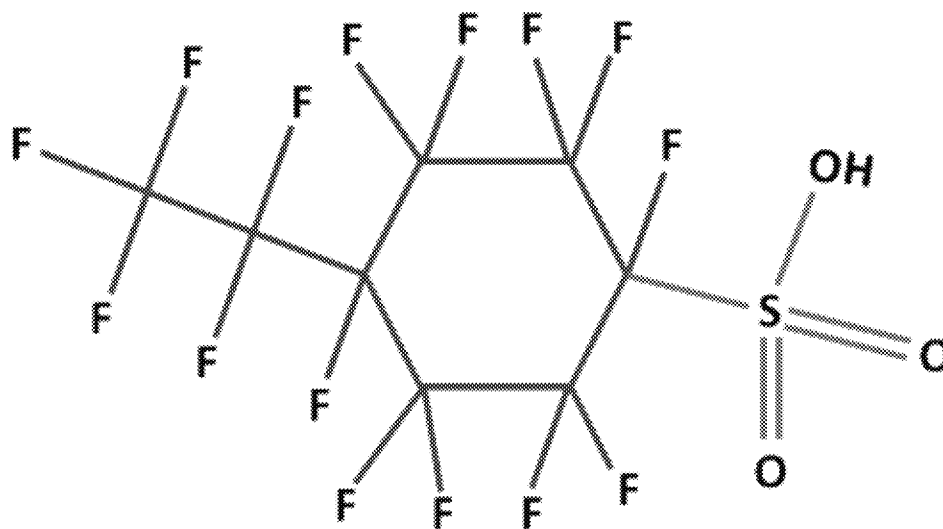
- perfluoroalkyl iodides (PFAIs) and perfluoroalkane aldehydes (PFALs), associated with the fluorotelomerization process
- perfluoroalkyl ether carboxylic acids (PFECAs) and perfluoroalkyl ether sulfonic acids (PFESAs)

As discussed in Section 2.4, some PFECAs have been developed or used as replacements for other PFAS that are phased out of production and use. This includes GenX chemicals (see text box). Other emerging fluorinated replacement PFECAs more recently detected in the environment, such as perfluoro-2-methoxyacetic acid (PFMOAA), are described in Sun et al. (2016).

### GenX Chemicals {TEXT BOX}

#### Figure 2-7. Example replacement chemistry structure for GenX Ammonium Salt.

In addition to linear and branched structures, certain cyclic structures have much in common with the non-cyclic PFAS, and are consistent with the definitions / descriptions provided above. As an example, Figure 2- # illustrates the structure of PFECHS (perfluoro-4-ethylcyclohexanesulfonate) which is a PFAS compound. It is used in airplane hydraulic fluids and has been found both in the environment (Kabore et al. 2018; Howard and Muir 2010; De Silvia et al. 2011; Lescord et al. 2015; Houde et al. 2016) and in human blood (Miaz et al. 2020). It is a non-aromatic compound with a sulfonate active group connected to a perfluorinated two-carbon tail by a fully fluorinated six-carbon ring. PFECHS fits the Buck et al. (2011) description by having a fully fluorinated aliphatic tail of one or more carbon atoms attached to a charged functional group head.



**Figure 2 - # Illustration of perfluoro-4-ethylcyclohexanesulfonate (PFECHS) Structure**

*Source: Michigan PFAS Action Response Team's Human Health Workgroup PFECHS Whitepaper (May 15, 2020)*

### 2.3.2 Analytical Developments

Early detection of PFAS in environmental media was hindered by the analytical capability challenges arising from the unique surface-active properties of PFAS (Giesy and Kannan 2001; 3M Company 2000b). Since the 2000s, methods have been, and continue to be, developed with lower detection limits (for example, parts per trillion (ppt)) in water, that are commensurate with levels of potential human health effects. More commercial laboratories now offer these analytical capabilities. Analytical methods continue to be developed and improved to test a variety of media and additional PFAS; these continue to improve our knowledge of PFAS in the environment and potential human health effects. For further information on analytical methods, refer to Section 11.

The list of PFAS that can be tested for has also evolved over time, with longer lists of compounds and changing commercial availability helping to drive the evolving health and environmental concerns. Early focus was on PFOA and PFOS, but nationwide testing of drinking water supplies under the USEPA's Third Unregulated Contaminant Monitoring Rule (UCMR3) led to four additional PFAAs (PFHpA, PFNA, PFBS, PFHxS) gaining greater attention. More information about UCMR3 is provided in Section 6.3, and a summary of the occurrence data for the six PFAAs analyzed during UCMR3 is provided in Section 8.2.2.2. In Germany, von der Trenck et al. (2018) presented health- and ecological-based PFAS significance thresholds for 7 of 13 priority PFAS for the assessment of contaminated groundwater.

Many state regulatory agencies now request or require testing for an expanded list of long- and short-chain PFAAs, and some potential precursors to PFAAs, such as fluorotelomers. Other polyfluoroalkyl substances are also receiving increased attention, as illustrated in Figure 2-14. Many of these PFAS are also summarized in Figure 2-4.

#### **Figure 2-14. Emerging awareness and emphasis on PFAS occurrence in the environment.**

Since the early 2000s, three analytical methods have been developed, validated, and published by USEPA for the analysis of PFAS in drinking water. In order of development, these include Methods 537, 537.1, and 533 (USEPA 2020). According to USEPA, these methods were developed for accuracy, precision, and robustness and have been through multi-lab validation and peer review. USEPA notes that Method 537 was used extensively during UCMR 3, described above. These methods were developed for finished drinking water from groundwater and surface water sources. Most recently (December 2019), USEPA published Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (USEPA 2019f). Method 533 includes additional PFAS analytes not included in Method 537.1, including shorter-chain PFAS and fluorotelomers. Methods 537.1 and 533 have both been validated for the analysis of HFPO-DA (a component of the GenX processing aid technology). For more information, refer to Section 11.2 – Analytical Methods/Techniques.

## References

- De Silva, A.O., et al., Detection of a cyclic perfluorinated acid, perfluoroethylcyclohexane sulfonate, in the Great Lakes of North America. *Environ Sci Technol*, 2011. 45(19): p. 8060-6.
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- USEPA, April 27, 2020, EPA PFAS Drinking Water Laboratory Methods: <https://www.epa.gov/pfas/epa-pfas-drinking-water-laboratory-methods>



ITRC PFAS Team forum post  
2-13-21

## PFAS Technical and Regulatory Guidance Document New Content – Team Review 2

Comments are due by the **end of the day on Friday 3/5** – upload your comment spreadsheet files on the team private page, Document Repository > PFAS TeamReview2 Comments folder.

Please do not circulate these draft materials beyond the ITRC PFAS Team.

The draft review materials can be downloaded from the team private page, Document Drafts > Team Review 2 folder. A Zip file containing all of the files is available. In addition, the individual files are posted in case you are not able to download a Zip file. The files included are:

- PFASTeamReview2.zip
- TeamReview2\_PFAS\_CommentSpreadsheet(2-12-21).xlsx
- PFAS\_Section2\_Rev2(2-12-21).PDF
- PFAS\_Figure\_2-3\_master\_for\_web\_pdf\_021221.PDF
- PFAS\_Section3\_Rev2(2-12-21).PDF
- Sec3\_TransitionTable-v1(2-12-21).xlsx
- Sec3\_AFFF\_Characteristics-v1(2-12-21).xlsx
- PFAS\_Section4\_Rev(2-12-21).PDF
- Sect4\_PhysChemProp\_Table\_February2021.xlsx
- PFAS\_Section5\_Rev2(2-12-21).PDF
- ITRC\_BCF-BAF\_compilation\_20210120\_DRAFT\_DO\_NOT\_CIRCULATE.xlsx
- PFAS\_Section7.1\_Rev(2-12-21).PDF
- PFAS\_Section8.2\_Rev(2-12-21).PDF
- Sec8\_PFAS\_Regulatory\_Programs\_Table(2-12-21).xlsx
- PFAS\_Section10\_Rev2(2-12-21).PDF
- PFAS\_Section11\_Rev(2-12-21).PDF
- Draft\_Table\_Data\_Usability\_PFAS\_January\_2021.PDF
- PFAS\_Section12\_Rev(2-12-21).PDF
- Integrated\_Water\_Treatment\_Flow\_Chart(2-12-21).PDF
- PFAS\_Section13\_Rev(2-12-21).PDF
- PFAS\_Leachate\_Additions\_to\_Table\_17.3\_Rev(2-12-21).PDF

We welcome comments from all team members – interested party and members, new and returning members. Please use the comment spreadsheet for all comments. Do not post marked-up copies of the documents. The spreadsheet includes an Instructions tab and separate tabs for comments on new content for each of the Tech Reg main sections that currently have drafts.

The review files include the text that is being revised or new text. They may not include all of the existing text surrounding the changes that is not being revised. If additional context for the change is needed, please refer to the web version of the Guidance Document, <https://pfas-1.itrcweb.org>.

We may have a few more files to add to this review. We will post when they are available.

If you have any questions, please email Lesley, [lhay\\_wilson@sagerisk.com](mailto:lhay_wilson@sagerisk.com).

Thank you to all the writing subgroups for your hard work!

Review Note: This file contains **new content for Section 2** of the PFAS Guidance Document (PFAS-1):

- Additions in Section 2.2 Chemistry, Terminology and Acronyms
- Revisions in Section 2.2.1 Naming Convention Considerations
- Revisions in Section 2.2.2 Introduction to the PFAS Family, Update to Figure 2-3 provided as a separate PDF.
- Revisions in 2.2.3.1. Perfluoroalkyl Acids (PFAAs)
- Revision in 2.2.4.2 Perfluoroalkane Sulfonamido Substances
- Revision in 2.2.4.3 Other Polyfluoroalkyl Substances, Figure 2-12 caption.
- New table in 2.3.2 Analytical Developments
- Additions in Section 2.5
- Revisions in Section 2.6.1.3 Metal Finishing and Plating

This file includes notes on revisions that were included in External Review 1. The writing subgroup is still considering the comments from External Review 1. Please focus this review on the new content. Please use the comments spreadsheet TeamReview2\_PFAS\_CommentSpreadsheet(2-12-2021).xlsx to provide your comments. Instructions are included in the spreadsheet. If additional context for the change is needed, please refer to the web version of the PFAS Technical and Regulatory Guidance Document, <https://pfas-1.itrcweb.org>.

## **2 PFAS Chemistry and Naming Conventions, History and Use of PFAS, and Sources of PFAS Releases to the Environment**

The PFAS Team developed two training module videos with content related to this section, they are the Naming Conventions and Physical and Chemical Properties video and the Production, Uses, Sources and Site Characterization video.

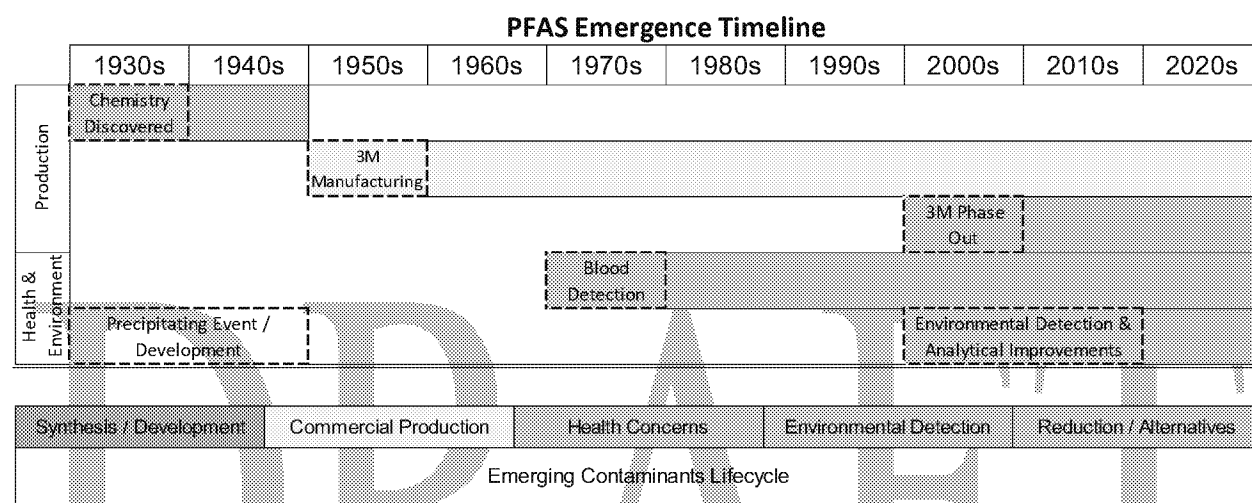
PFAS chemistry was discovered in the late 1930s. Since the 1950s, many products commonly used by consumers and industry have been manufactured with or from PFAS, as the unique physical and chemical properties of PFAS impart oil, water, stain, and soil repellency, chemical and thermal stability, and friction reduction to a range of products. These products have application in many industries, including the aerospace, semiconductor, medical, automotive, construction, electronics, and aviation industries, as well as in consumer products (such as carpets, clothing, furniture, outdoor equipment, food packaging), and firefighting applications (3M Company 1999a; Buck et al. 2011; KEMI 2015a; USEPA 2017b).

The number of PFAS and their uses have expanded over the years. It has been estimated that the PFAS family may include approximately 5,000–10,000 chemicals (USEPA 2018i). A recent inventory of PFAS identified Chemical Abstracts Service (CAS) Registry Numbers for more than 4,700 PFAS that could have been, or may be, on the global market (OECD 2018), although the uses of each of these PFAS may not be known (KEMI 2015a). Publicly available health and toxicity studies are limited to only a small fraction of these PFAS, and modern commercially available analytical technologies typically identify only about 20–30 PFAS.

Scientific, regulatory, and public concerns have emerged about potential health and environmental impacts associated with chemical production, product manufacture and use, and

disposal of PFAS-containing wastes. These concerns have led to efforts to reduce the use of or replace certain PFAS, such as the two most widely produced, commonly encountered, and most studied compounds: perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (USEPA 2016c; WA DER 2017).

<External Review 1 change>PFAS have followed a similar pattern of emergence and awareness exhibited by many other anthropogenic environmental contaminants. The following graphic (Figure 2-1) provides a general timeline of PFAS emergence and awareness that includes categories of 1) Synthesis/Development, 2) Commercial Production, 3) Health Concerns, 4) Environmental Detection, and 5) Reduction / Alternatives.



**Figure 2-1. General timeline of PFAS emergence and awareness.**

*Graphic is intended to provide a general sense of PFAS emergence and awareness by decade. It is not intended to be exhaustive or precise.*

*Source: J. Hale, Parsons. Used with permission.*

The objective of this section is to lay a foundation for identifying potential PFAS sources in the environment.

## 2.1 Environmental Significance

PFAS have been and still are widely used, but not all types and uses of PFAS result in the same level of environmental impact and exposure. When considering potential environmental impacts from PFAS, it is critical to be as specific as possible not only about the particular PFAS involved, but also where and how they are released to the environment. For example, a stable, insoluble fluoropolymer such as polytetrafluoroethylene (PTFE) may pose little environmental or health risk once it is in a product, but potentially significant environmental releases may occur if controls are not used during PTFE manufacturing, when nonpolymer PFAS, such as PFAAs, are used to make the PTFE. Such considerations may help to focus investigation resources on major sources.

Figure 2-1 illustrates a conceptual PFAS lifecycle beginning at PFAS synthesis (raw materials). These raw materials are then used in a variety of manufacturing processes and industrial/commercial applications to create commercial and consumer products that contain or were treated with PFAS. Throughout this life cycle, variable types and amounts of PFAS may be released to the environment from manufacturing waste streams, fugitive emissions, spills, disposal of PFAS-containing or -treated materials, and general wear and tear of consumer products. Sometimes the intended use of the PFAS product (for example, firefighting foams) requires direct release to the environment. PFAS from a host of sources also may be aggregated in wastewater treatment plant effluent and sludges, creating secondary release sources. The volume, concentration, and mixture of PFAS released to the environment varies based on the source (process, material, or product), release mechanism(s), and environmental controls employed throughout this life cycle. Exposure to PFAS may occur as (1) direct interaction with the manufacturing process, (2) professional or intensive use of PFAS-containing materials, (3) use of or contact with commercial and consumer products containing PFAS, or (4) exposure (human or ecological) to environmental media that has been impacted by PFAS. The relative significance of these exposures will also vary widely.

**Figure 2-1. Generalized PFAS uses and relative exposure and environmental impact potential from PFAS life cycle.**

This figure is not exhaustive with regard to all sources or release mechanisms from those sources. Multiple sources may exist at a site, and the relative potential of exposure and environmental impact may vary based on several considerations.

Due to the widespread use of PFAS in commercial and consumer products, other minor point and diffuse releases of PFAS to the environment may occur during use and disposal of some PFAS-containing products. Although these may result in locally significant environmental impacts, these releases typically affect smaller geographic areas and have lower total PFAS mass than major sources, such as PFAS chemical manufacturing, PFAS use in certain industries, and application of certain firefighting foams.

Different PFAS products and sources differ in their relative environmental significance, volumes released, distribution mechanisms, area affected, and relative concentration of impacted media. For instance, application of Class B firefighting foam may impact a moderate area relative to air dispersion from fluoropolymer production, but may exhibit higher associated groundwater concentrations near the source area.

The type of PFAS involved also determines the relative environmental significance. Nonpolymer PFAS (both per- and polyfluorinated) and some side-chain fluorinated polymer PFAS are likely to pose greater risks when released to the environment than certain fluoropolymer sources, such as the fluoropolymers PTFE, fluorinated ethylene-propylene (FEP), perfluoroalkoxy polymer (PFA), and ethylene tetrafluoroethylene (ETFE). These fluoropolymers are considered to be polymers of low concern (Section 2.2.2.1) because they are relatively stable, insoluble in the environment, and not bioavailable (Henry et al. 2018). However, environmental impact from the production or manufacturing uses of some fluoropolymers can pose a significant risk if emissions are not properly controlled at the industrial site. Also, releases to the environment from the disposal of fluoropolymers cannot be ruled out, as nonpolymer PFAS (such as the PFAAs used as polymerization aids) may be found at trace levels as impurities and byproducts in

some fluoropolymer products (3M Company 1999a). Research suggests side-chain fluorinated polymers and fluorotelomer-based polymers are likely to break down into nonpolymer PFAS with time (Li et al. 2018; Washington et al. 2018), although it is documented that one fluoropolymer (PTFE) did not degrade to significant levels of PFAAs during incineration (Aleksandrov et al. 2019).

Finally, another consideration regarding environmental impacts is the issue of anthropogenic (human-caused, not naturally occurring) ambient or “background” levels of PFAS. As discussed in Section 6, the long duration of PFAS use and their release from many types of sources may have resulted in low-level contamination of environmental media worldwide. The implications of such ambient levels of PFAS should be considered in evaluating exposures and risk levels, establishing site action levels and cleanup goals, and identifying PFAS sources.

## 2.2 Chemistry, Terminology, and Acronyms

This section focuses on chemistry, terminology, names, and acronyms for those PFAS most commonly reported in the environment, identified in scientific literature, and those PFAS most commonly tested for by current analytical methods. Other important classes of PFAS are introduced. This section also introduces the chemical manufacturing processes that influence the types of PFAS that are found in the environment.

PFAS are characterized by carbon atoms that are linked together with fluorine atoms attached to the carbons. <External Review 1 change>An early and widely recognized technical definition of PFAS is provided by Buck et al. (2011) who define PFAS as, “highly fluorinated aliphatic substances that contain one or more carbon (C) atoms on which all the hydrogen (H) substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by fluorine (F) atoms, in such a manner that they contain the perfluoroalkyl moiety  $C_nF_{2n+1}-$ ” (Buck et al. 2011).

The definition of PFAS may evolve to reflect continued study of these compounds. For example, the definition of PFAS used in one study (OECD 2018) also included chemicals that contain –  $C_nF_{2n}$  – in addition to the  $C_nF_{2n+1}-$ , which includes chemicals with both ends of the carbon-fluorine chain connected to a functional group, such as cyclic analogs of linear PFAS.

<External Review 1 change>More recently, the Michigan PFAS Action Response Team (MPART) offers a working description of perfluoroalkyl substances, stating that the basic chemical structure is a chain (or tail) of two or more adjacent carbon atoms with a charged functional group head attached at one end. The functional groups commonly are carboxylates or sulfonates, but other forms are also detected in the environment. For a linear or branched aliphatic tail, this structure can be written as:  $C_nF_{2n+1}-R$  where “ $C_nF_{2n+1}$ ” defines the length of the perfluoroalkyl chain tail, “n” is  $\geq 2$ , and “R” represents the attached functional group head. The tail may be linear, or branched, or contain a cyclic portion, but it always contains adjacent fluorinated carbon atoms in a  $C_nF_{2n+1}$  moiety (with  $n \geq 2$ ). The functional group may contain one or more carbon atoms, which are included in the total number of carbons when naming the compound.

<New>Polyfluoroalkyl substances are distinguished from perfluoroalkyl substances by not being fully fluorinated. Instead, they have a non-fluorine atom (typically hydrogen or oxygen)

attached to at least one, but not all, of the carbon atoms in the tail, while at least two adjacent of the remaining carbon atoms in the tail are fully fluorinated.

Gluge, Jj., et al. (2020) acknowledge the Buck and OECD definitions while also considering the definition of PFAS to include:

- substances where a perfluorocarbon chain is connected with functional groups on both ends
- aromatic substances that have perfluoroalkyl moieties on the side chains
- fluorinated cycloaliphatic substances.

<External Review 1 change>Whether or not the presence of an aromatic component still constitutes classification as PFAS remains a subject of discussion.

For practical reference, the USEPA CompTox chemical dashboard provides useful information about multiple PFAS known to USEPA.

## General Concepts of Organofluorine Chemistry for PFAS

*Organofluorine Chemistry: A branch of organic chemistry involving organic molecules with a carbon-fluorine bond. Organofluorine molecules have many commercial uses. They include PFAS, such as PFOA, shown below:*

*EXAMPLE: 3D model of a PFOA (perfluorooctanoic acid) molecule, in its acid form.*

*Source: Manuel Almagro Rivas (Own work using: Avogadro, Discovery Studio, GIMP) [CC BY-SA 4.0] (<https://creativecommons.org/licenses/by-sa/4.0/>), via Wikimedia Commons. <https://commons.wikimedia.org/wiki/File:PFOA-3D.png>*

*Dark gray spheres represent carbon atoms linked together in a chain; there are eight of them, so “octane” is used in the name. Green spheres represent fluorine atoms bonded to carbon atoms. Red spheres represent oxygen atoms. White sphere represents a hydrogen atom that dissolves away in water, which makes this an acid. Fluorine atoms are attached to all possible bonding sites, making this perfluorinated. If some of the fluorine atoms were replaced by other atoms (such as oxygen or hydrogen), it would be polyfluorinated. Without the hydrogen, the “head end” takes on a negative charge and can bond to things through electrostatic attraction. The fluorine “tail end” is strong and stable, giving it lipid- and water-repelling properties, but also making it persistent in the environment.*

*Isomer: A molecule with the same molecular formula as another molecule, but with a different chemical structure. Isomers contain the same number of atoms of each element, but have different arrangements of their atoms. See Figure 2-13 for an example; linear and branched PFOS contain the same number of carbon, fluorine, oxygen, and sulfur atoms, but these atoms are arranged differently depending on whether it is a linear or branched isomer of PFOS.*

*Homologue Groups and Homologous Series: A group of organic compounds, usually listed in order of increasing size, that has a similar structure (and therefore also similar properties) and whose structures differ only by the number of carbon atoms in the chain. For example, all of the linear and branched isomers of PFOS would be in the C8 homologue group, while all of the*

linear and branched isomers of perfluorohexane sulfonic acid (PFHxS) would be in the C6 homologue group. The C4-C12 PFASs are a homologous series of perfluorosulfonates.

### 2.2.1 Naming Convention Considerations

*<Text Box> “PFAS,” not “PFASs”: The acronym “PFAS” stands for “per- and polyfluoroalkyl substances.” No single chemical within the PFAS family can be both perfluorinated and polyfluorinated, so by definition “PFAS” is plural and a small “s” is not needed. Some authors elect to add a small “s” to this acronym (PFASs) to emphasize the fact that it is plural, but it is not needed. When referring to a single chemical within the PFAS family, it is more accurate to simply name that specific chemical.*

There is confusion among the environmental community and the public due to overgeneralization when describing PFAS and the lack of consistent naming of specific PFAS. The use of consistent naming conventions would reduce confusion and support clearer communication (Buck et al. 2011) (Wang, DeWitt, et al. 2017).

*<Text Box> The use of nonspecific acronyms, such as perfluorinated compound (PFC), has hampered clarity of investigative results. The acronym “PFC” is poorly defined in the scientific literature, but typically refers to “perfluorinated compounds.” It does not include “polyfluorinated substances,” which are increasingly recognized as important contaminants at many PFAS sites.*

~~<Delete this has been addressed in update in section 2.2> NOTE Consistent naming also helps to distinguish PFAS from other organic compounds that contain fluorine. As defined in the literature, PFAS include only fluorinated aliphatic (carbon chain) substances. PFAS do not include fluorinated compounds that contain aromatic (carbon ring) features in their structures (for example, active pharmaceutical ingredients, crop protection agents, or chlorofluorocarbons (refrigerants)). This definition distinguishes PFAS from the more generic term “PFC,” which can include aromatic compounds.~~

~~In the future, it may be necessary to expand the current naming conventions and acronym approaches to ensure that standardized naming is available for additional members of the PFAS family of compounds. Buck et al. (2011) is an open-access paper that provides a more detailed explanation of PFAS terminology, classification, and origins, and recommends specific and descriptive terminology, names, and acronyms for PFAS.~~

Chemicals in the PFAS family can exist in various ionic states (for example, acids, anions, cations), which have important implications for their chemical and physical properties. In most cases for PFAAs, this section uses the anionic form of a given PFAS name, as this is the state in which most PFAAs exist in the environment.

CAS numbers are another helpful tool for clearly identifying the chemical that is being referenced; however, care must be taken in selecting the correct CAS number to avoid confusion regarding the chemistry and behavior of the chemical being described. Some PFAS may occur in various ionic states, such as acids, anions (negatively charged), cations (positively charged), and zwitterions (both positively and negatively charged dipolar molecules), and each has its own CAS number (and some have no CAS number). The ionic state determines electrical charge and



physical and chemical properties, which in turn control fate and transport in the environment and potential human health and ecological effects. The ionic state of individual PFAS can result in significantly different physical and chemical properties, such as solubility, volatility, and bioaccumulative potential.

## 2.2.2 Introduction to the PFAS Family

PFAS encompass a wide universe of substances with very different physical and chemical properties (Section 4). ~~including gases (for example, perfluorobutane), liquids (for example, fluorotelomer alcohols), and solid material high-molecular weight polymers (for example, PTFE). For this reason, it is helpful to group PFAS that share similar chemical and physical properties.~~

As shown in Figure 2-2, the PFAS family may be divided into two primary classes: polymers and nonpolymers. Each class may contain many subclasses, groups, and subgroups, some of which are shown in the figure. This document focuses primarily on those nonpolymer PFAS most commonly detected in the environment and those PFAS that may be significant as “precursors” that can transform to more persistent forms.

**Figure 2-2. The PFAS family.** ~~< Add Family Hierarchy legend from the family tree to this figure>~~

The family tree is further expanded in Figure 2-3, based on nomenclature provided in Buck et al. (2011), Organization for Economic Co-operation and Development OECD (2015b), and Wang, DeWitt, et al. (2017), with further introduction to some of these chemicals provided later in this section.

Future updates to the family tree and nomenclature are expected to be necessary given the evolving public knowledge of these compounds. For example, other PFAS without analytical standards are being identified using nontarget analyses by research laboratories (Section 11). These PFAS do not necessarily have an associated CAS number but are being identified by molecular structure.

~~<External Review 1 change> Figure 2-3 is not inclusive of all PFAS and is intended to categorize a sampling of common PFAS chemistries. Additionally, as more information becomes available it is likely that there will be changes, until that time, we are sharing a traditional view of the PFAS Family and is based on the information shared in the before mentioned references.~~

~~An example of evolving classification includes whether perfluoropolyethers (PFPE) should be regarded as polymers or non-polymers, since this chemical group can function (or be used) as either a polymer or a non-polymer depending on the chemical structure (ionic character) and their intended use. These chemicals are often referred to as “Functionalized PFPE”. It is recommended this chemical category be carefully evaluated and not assume that all of the PFPE chemistries will fall into either the polymer or non-polymer classification.~~

~~Functionalized PFPE as a polymer, or Polymeric PFPE, can be used as a grease, solvent or lubricant. They are very large molecules (high molecular weight) and thereby tend to not be bioavailable and stable (not mobile) in the environment. They may have end groups that are~~

significantly smaller, as compared to the length of the repeating units (backbone) and have little to no polar effect (not polarized).

Functionalized PFPE as a non-polymer, can be used as a surfactant, soap or de-greaser. They are small (low molecular weights) making them more available for bioaccumulation and mobility in the environment. These chemistries have ionic end-groups (heads) which are used to capture or link together like-particles. An example of a Functionalized PFPE non-polymer would be ADONA and GenX. Please see Buck et al (2011) (pages 532-533) for more information on PFPE.

**Figure 2-3. PFAS family tree.** < A separate draft updated Figure 2-3 is available for Team Review 2>

Adapted from a graphic provided courtesy of Paul Caprio, EA Engineering.

A stand-alone PDF version of Figure 2-3 is available.

### 2.2.2.1 Polymer PFAS

Polymers are large molecules formed by combining many identical smaller molecules (or monomers (which are shorter chain molecules with no repeating units)) in a repeating pattern. Oligomers are smaller polymers, with relatively fewer repeating units.

The PFAS polymer class includes fluoropolymers, polymeric perfluoropolyethers, and side-chain fluorinated polymers (Henry et al. 2018; Buck et al. 2011; Wang, Cousins, et al. 2013):

- Fluoropolymers contain a carbon-only polymer backbone with fluorines directly attached to the carbon. Fluoropolymers include polymers like PTFE, ETFE, copolymer FEP, and PFA, which were historically made using ammonium perfluorooctanoate (APFO) or sodium perfluorooctanoate (NaPFO), which are salts of perfluorooctanoate (PFOA). Fluoropolymers also include polyvinylidene fluoride (PVDF), which was historically made using ammonium perfluoronanoate (APFN), the ammonium salt of perfluoronanoate (PFNA) (OECD 2015b), (Buck et al. 2011).
- The specific fluoropolymers PTFE, FEP, ETFE, and PFA have been referred to as “polymers of low concern” because they have high molecular weight and are extremely stable. PTFE has been demonstrated to not be bioavailable (Henry et al. 2018). Based on this, Henry et al. (2018) suggest polymers of low concern should be considered separately from other PFAS when evaluating risk. Polymers of low concern are reported to pose little environmental or health risk once in a consumer product.
- Polymeric perfluoropolyethers (PFPE) contain a carbon and oxygen polymer backbone with fluorines directly attached to carbon. Relatively little is known about these chemicals in the environment.
- Side-chain fluorinated polymers contain a nonfluorinated polymer backbone, off of which fluorinated side chains branch. These PFAS include fluorinated urethane polymers, fluorinated acrylate/methacrylate polymers, and fluorinated oxetane polymers. Some side-chain fluorinated polymers may become precursors for PFAAs, Section 2.2.3.1, when the point of connection of a fluorinated side chain on a polymer is broken to release a PFAA.

During the manufacture and manufacturing uses of some fluoropolymers, controls are necessary to mitigate potential releases of nonpolymer PFAS. Nonpolymer PFAS may be used as processing aids in the manufacture of some fluoropolymer PFAS, and may be found as impurities in some fluoropolymer products, and due to potential degradation of some fluoropolymers (3M Company 1999b; CalEPA 2018; Washington et al. 2018), see also Section 5.4.5.

#### 2.2.2.2 Nonpolymer PFAS

Nonpolymer PFAS encompass two major subclasses: perfluoroalkyl substances and polyfluoroalkyl substances, which include many groups and subgroups of chemicals. Figure 2-4 provides general classification and chemical structures, examples of each group, and examples of the primary uses of the nonpolymer PFAS highlighted in Figure 2-2 and Figure 2-3.

Nonpolymer PFAS were selected as the focus of this document because:

- they are the PFAS most commonly detected (to date) in humans, biota, and other environmental media and appear to be relatively more abundant at PFAS investigation sites (Section 6)
- data may be available regarding potential human health and ecological effects from environmental exposure for some of these chemicals (Section 7)
- state or federal standards or guidance values may exist for some of these chemicals (Section 8)
- they are included in most laboratory PFAS analyte lists (Section 11).

**Figure 2-4. Nonpolymer PFAS subclasses discussed in this document.** < Add Family Hierarchy legend from the family tree to this figure>

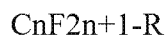
Source: Adapted with permission from Buck, R.C., J. Franklin, U. Berger, J. M. Conder, I. T. Cousins, P. de Voogt, A. A. Jensen, K. Kannan, S. A. Mabury, and S. P. van Leeuwenet. 2011. “Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins.” Integrated Environmental Assessment and Management, 7:513-541. Open access. Copyright 2011 SETAC. <http://dx.doi.org/10.1002/ieam.258>

#### 2.2.3 Perfluoroalkyl Substances

Perfluoroalkyl substances are fully fluorinated alkane molecules that include (but are not limited to):

- perfluoroalkyl acids (PFAAs) and
- perfluoroalkane sulfonamides (FASAs).

The basic chemical structure is a chain (or tail) of two or more carbon atoms with a charged functional group (or head) attached at one end. The functional groups commonly are carboxylates or sulfonates, but other forms are also detected in the environment. Fluorine atoms are attached to all possible bonding sites along the carbon chain of the tail, except for one bonding site on the last carbon where the functional group head is attached. This structure, which is illustrated in Figure 2-5 for PFOS and PFOA, can be written as:



where “ $\text{C}_n\text{F}_{2n+1}$ ” defines the length of the perfluoroalkyl chain tail, “ $n$ ” is  $>2$ , and “ $\text{R}$ ” represents the attached functional group head. Note that the functional group may contain one or more carbon atoms, which are included in the total number of carbons when naming the compound.

**Figure 2-5. The tail and head structure of PFOS and PFOA molecules.**

### 2.2.3.1 Perfluoroalkyl Acids (PFAAs)

PFAAs are some of the least complex PFAS molecules. They are essentially non-degradable under normal environmental conditions. Biotic and abiotic degradation of many polyfluoroalkyl substances may result in the formation of PFAAs. As a result, PFAAs are sometimes referred to as “terminal PFAS” or “terminal degradation products,” meaning no further degradation products will form from them under environmental conditions. Polyfluoroalkyl substances that degrade to create terminal PFAAs are referred to as “precursors.” Longer chain PFAAs do not degrade to shorter chain PFAAs.

The PFAA group is divided into two major subgroups (as shown in Table 2-1 and Figure 2-3).

- Perfluoroalkyl carboxylic acids (PFCAs), or perfluoroalkyl carboxylates, are used commercially and can be formed as terminal degradation products of select precursor polyfluoroalkyl substances, such as FTOHs. An example PFCA is PFOA.
- Perfluoroalkane sulfonic acids (PFSAs), or perfluoroalkane sulfonates, also are used commercially and can be formed as terminal degradation products of select precursor polyfluoroalkyl substances, such as perfluoroalkyl perfluoroalkane sulfonamide ethanols (FASes/PFOSEs). An example PFSA is PFOS.

Other subgroups of PFAAs are introduced in Section 2.2.3.3. Some of those are compounds that are receiving increasing attention, are being added to commercial laboratory target analyte lists, and are being detected in the environment.

PFAAs are the group of PFAS that make up the majority of PFAS typically included in commercial laboratory target analyte lists and are the primary PFAS for which federal or state health-based guidance values have been established. As a result, PFAAs tend to drive site investigation and remediation decisions, so it is helpful to understand the naming conventions for this class. Many of the commonly detected PFAAs are denoted using the structural shorthand:

PFX<sub>Y</sub> where:

PF = perfluoro

X = the carbon chain length (using the same naming conventions as hydrocarbons based on the number of carbons (for example, B for butane or 4 carbons, Pe for pentane or 5 carbons))

Y = the functional group (for example, A = carboxylate or carboxylic acid and S = sulfonate or sulfonic acid)

Table 2-1 illustrates how this naming structure works for the PFCAs and PFSAAs, which collectively are referred to as PFAAs.

**Table 2-1. Basic naming structure and shorthand for PFAAs** <Capitalize ‘Carboxylate’ in Row 1 Column Y>

Note that for PFCAs, the total number of carbons used for naming the compound includes the carbon in the carboxylic acid functional group (COOH). For example, although PFOA has seven carbons in its fluoroalkyl tail, all eight of the carbons in the molecule are used to name it, hence perfluorooctanoate. But in terms of chemical behavior, PFOA would be more analogous to seven-carbon perfluoroheptane sulfonate (PFHpS) than to eight-carbon perfluorooctane sulfonate (PFOS).

Table 2-1 shows the PFAA names and formulas in both the anionic (also referred to as “deprotonated” or negatively charged) and acid (also referred to as protonated or neutral) forms. The anionic form is the state in which PFAAs are found in the environment, except in very rare situations (for example, extremely low pH). The anionic and acid forms of PFAA names are often incorrectly used interchangeably (for example, perfluorooctane sulfonate and perfluorooctane sulfonic acid), and the same acronym (in this case, PFOS) applies to both forms. However, as discussed below and in Section 4, their physical and chemical properties are different, and it is important to know which form is being described.

Until recently, PFCAs and PFSAAs have been the subgroups most commonly tested for in the environment; however, a wide range of PFAS with other functional groups exists for which the same “PFXY” shorthand shown above may or may not apply. For naming conventions for these compounds, please refer to Buck et al. (2011).

### 2.2.3.2 Long-Chain Versus Short-Chain Distinction

PFAS, predominantly PFAAs, are sometimes described as long-chain and short-chain as a shorthand way to categorize PFCAs and PFSAAs that may behave similarly in the environment; however, it is important not to generalize about PFAA behavior based only on chain length. As recent research suggests, other factors besides chain length may affect bioaccumulation potential of PFAS (Ng and Hungerbühler 2014).

According to the OECD (2013):

- Long-chain refers to:
  - PFCAs with eight or more carbons (seven or more carbons are perfluorinated)
  - PFSAAs with six or more carbons (six or more carbons are perfluorinated)
- Short-chain refers to:
  - PFCAs with seven or fewer carbons (six or fewer carbons are perfluorinated)
  - PFSAAs with five or fewer carbons (five or fewer carbons are perfluorinated)

Table 2-2 illustrates the differences in the short-chain and long-chain PFCAs and PFSAAs.

**Table 2-2. Short-chain and long-chain PFCAs and PFSAs****Anions Versus Acids**

As noted above, the names for the anionic and acid forms of PFAAs are often used interchangeably, but it is critical to know which form is being discussed because of differences in their physical and chemical properties and behavior in the environment (Section 6). Some important things to keep in mind regarding the anionic versus acid forms are:

- Most PFAAs are present in environmental and human matrices in their anionic form. For example, PFOS is present in the environment in the anionic form, perfluorooctane sulfonate.
- Although laboratories may be reporting PFOA or PFOS using the acid form of their name, they are actually measuring the anionic form (for example, perfluorooctanoate or perfluorooctane sulfonate), as this is the form that exists in the environment.
- The acid form and their associated cationic salts have CAS numbers, while the anionic forms may not (Table 2-1). For example, PFOS can exist as different salts (cationic), including sodium, lithium, potassium, or ammonium. Each of these salts will have a different CAS number:
  - PFOS, acid form CAS No.: 1763-23-1
  - PFOS, potassium salt CAS No.: 2795-39-3
  - PFOS, ammonium salt CAS No.: 29081-56-9
- When the salt or acid exists in water or other liquids, it will dissociate (lose its hydrogen atom), and the salt or acid will break off and form the anion (for example, COO<sup>-</sup> or SO<sub>3</sub><sup>-</sup>). Figure 2-6 illustrates the dissociation of PFBA.

**Figure 2-6. Dissociation of PFBA.**

- It is most important to distinguish between the acid form and anionic form when reporting the physical and chemical properties. The discussion of PFAS properties in this guidance document generally refers to the anionic form; it will be specifically called out if the acid form is being discussed.

**A Note About PFAS Naming in Laboratory Reports (see Section 11)**

*Even though PFAAs occur as anions in the environment, some laboratories report all of their results in the acidic form, while others may report PFCAs as acids (for example, perfluorooctanoic acid) and PFSAs as anions (for example, perfluorooctane sulfonate). Different naming conventions in laboratory reports have led to confusion regarding exactly which form of the PFAA the labs are measuring. Although the lab is measuring the concentration of PFAA anions present in the sample, where the results are reported as an acid, the lab has adjusted for the H<sup>+</sup> cation (which has so little mass, this does not affect the resulting concentration). It should be noted that the standards used by laboratories to perform analyses may be prepared from PFAA salts, as is often the case for sulfonate standards. If so, the lab must adjust the reported concentration to account for the mass of the counterion (typically Na<sup>+</sup> or K<sup>+</sup>). The*

calculation to do this is described in Section 7.2.3 of EPA Method 537 (Shoemaker, Grimmer, and Boutin 2009).

### 2.2.3.3 Other PFAAs

Other PFAAs include:

- perfluoroalkyl sulfinic acids (PFSiAs), associated with the electrochemical fluorination (ECF) process and also occur as intermediate environmental transformation products
- perfluoroalkyl phosphonic acids (PFPAs) and phosphinic acids (PFPiAs), associated with the fluorotelomerization process and used as surfactants

### 2.2.3.4 Perfluoroalkane Sulfonamides (FASAs)

FASAs, such as perfluorooctane sulfonamide (FOSA), are used as raw material in the ECF process to make perfluoroalkyl sulfonamide substances that are used for surfactants and surface treatments. FASAs can degrade to form PFAAs such as PFOS.

### 2.2.3.5 Other Perfluoroalkyl Substances

Other perfluoroalkyl substances shown on Figure 2-3 include:

- perfluoroalkane sulfonyl fluorides [PASFs, such as perfluorooctane sulfonyl fluoride (POSF) and perfluorobutane sulfonyl fluoride (PBSF)], and perfluoroalkanoyl fluorides (PAFs), associated with the ECF process
- perfluoroalkyl iodides (PFAIs) and perfluoroalkane aldehydes (PFALs), associated with the fluorotelomerization process
- perfluoroalkyl ether carboxylic acids (PFECAs) and perfluoroalkyl ether sulfonic acids (PFESAs)

As discussed in Section 2.4, some PFECAs have been developed or used as replacements for other PFAS that are phased out of production and use. This includes GenX chemicals (see text box). Other emerging fluorinated replacement PFECAs more recently detected in the environment, such as perfluoro-2-methoxyacetic acid (PFMOAA), are described in Sun et al. (2016).

### GenX Chemicals

A PFECA, commonly referred to by the trade name “GenX,” has been used by one manufacturer as a replacement for APFO (PFOA) as a surfactant and polymerization aid in the production of their PTFE product. GenX actually refers to the GenX processing aid technology, while the major chemicals used include:

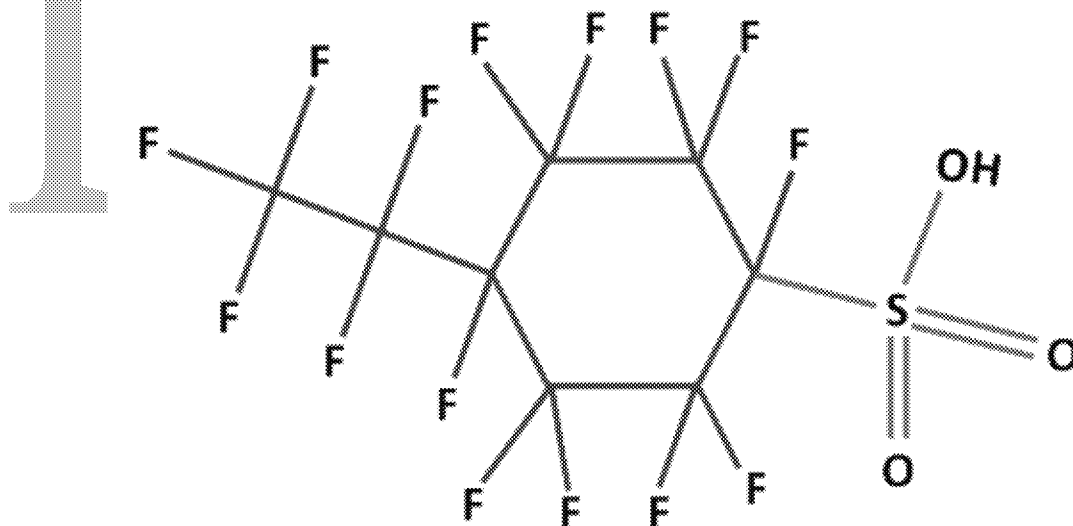
hexafluoropropylene oxide (HFPO) dimer acid (HFPO-DA, CAS No. 13252-13-6, also known as 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid [PFPrOPrA] or FRD-903) and its ammonium salt (ammonium, 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoate [CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>OCF(CF<sub>3</sub>)COO–NH<sub>4</sub><sup>+</sup>, CAS No. 62037-80-3, also known as FRD -902]) (Wang, Cousins, et al. 2013) (Buck 2015) (USEPA 2018d).

Prior to their use in PTFE production, GenX chemicals were produced as a byproduct of other manufacturing processes (NC DEQ 2018). HFPO also is used to manufacture other HFPO-DA derivatives, fluoropolymers (including polyethers), and other specialty agrochemical, semiconductor, and pharmaceutical applications (ATSDR 2018e). HFPO-trimer acid and longer polymer fluorides can be formed from reaction of HFPO-DA.

Further discussion of the GenX chemicals is provided in Section 2.4.6. The chemical structure of the ammonium salt is shown in Figure 2-7.

**Figure 2-7. Example replacement chemistry structure for GenX Ammonium Salt.**

<External Review 1 change> In addition to linear and branched structures, certain cyclic structures have much in common with the non-cyclic PFAS, and are consistent with the definitions / descriptions provided above. As an example, PFECHS (perfluoro-4-ethylcyclohexanesulfonate) is a PFAS compound. It is used in airplane hydraulic fluids and has been found both in the environment (Kaboré et al., 2018; Howard and Muir, 2010; De Silvia et al., 2011; Lescord et al., 2015; and Houde et al., 2016) and in human blood (Miaz et al., 2020). It is a non-aromatic compound with a sulfonate active group connected to a perfluorinated two-carbon tail by a fully fluorinated six-carbon ring. PFECHS fits the Buck et al (2011) description by having a fully fluorinated aliphatic tail of one or more carbon atoms attached to a charged functional group head. PFECHS is considered a PFSA and is an analog of PFOS.



**Figure 2 - # Illustration of perfluoro-4-ethylcyclohexanesulfonate (PFECHS) Structure**

Source: Michigan PFAS Action Response Team's Human Health Workgroup PFECHS  
Whitepaper (May 15, 2020)

## 2.2.4 Polyfluoroalkyl Substances



Polyfluoroalkyl substances and some side-chain fluorinated polymers are increasingly being identified as important to understanding the occurrence, fate, and transport of PFAS at release sites and in the environment (OECD 2013; Butt, Muir, and Mabury 2014; Liu and Mejia Avendaño 2013; Wang et al. 2011; Mejia-Avendaño et al. 2016). Figure 2-2 and Figure 2-3 highlight the groups of polyfluoroalkyl substances that, to date, have most commonly been detected at PFAS sites (see Barzen-Hanson et al. 2017; OECD 2018) indicates that of the approximately 4,700 PFAS identified in that study, about 90% were potential precursors to PFAAs.

Polyfluoroalkyl substances are distinguished from perfluoroalkyl substances by not being fully fluorinated. Instead, they have a nonfluorine atom (typically hydrogen or oxygen) attached to at least one, but not all, carbon atoms, while at least two or more of the remaining carbon atoms in the carbon chain tail are fully fluorinated (Figure 2-4).

The carbon-hydrogen (or other nonfluorinated) bond in polyfluoroalkyl molecules creates a “weak” point in the carbon chain that may be susceptible to biotic or abiotic degradation. As a result, many polyfluoroalkyl substances that contain a perfluoroalkyl  $C_nF_{2n+1}$  group are potential precursor compounds that have the potential to be transformed into PFAAs.

Figure 2-8 provides examples of degradation pathways for environmentally relevant polyfluoroalkyl precursors derived from two PFAS production methods, fluorotelomerization and ECF, respectively (Buck et al. 2011; Liu and Mejia Avendaño 2013; Butt, Muir, and Mabury 2014). Note that these figures include some PFAS not discussed in this guidance document, but described in Buck et al. (2011). Refer to Section 5.4, for further information on transformation processes, noting that not all degradation products will be formed through every environmental transformation process.

**Figure 2-8. Example polyfluoroalkyl substance degradation pathways.**

*(Note that degradation of POSF-based products is for the terrestrial environment, but transformation into lower homologues of PFCAs and PFSAAs in the atmosphere is also possible.)*

**2.2.4.1 Fluorotelomer Substances**

Fluorotelomer substances are polyfluoroalkyl substances produced by the fluorotelomerization process. As shown in Figure 2-8, the degradation of fluorotelomer-based substances is a potential source of PFCAs in the environment, but not PFSAAs (Buck et al. 2011).

Fluorotelomer-based polyfluoroalkyl substances are named using an “n:x” prefix where “n” indicates the number of fully fluorinated carbon atoms ( $n > 2$ ) and “x” indicates the number of carbon atoms that are not fully fluorinated ( $x > 1$ ). An example of a polyfluoroalkyl substance is shown in Figure 2-9, which also illustrates the “n:x” naming convention.

**Figure 2-9. Example of a polyfluoroalkyl substance.**

The following fluorotelomer substances are those most commonly detected in the environment to date (Section 6):

- Fluorotelomer alcohols (FTOH): The n:2 fluorotelomer alcohols (n:2 FTOHs) are key raw materials in the production of n:2 fluorotelomer acrylates and n:2 fluorotelomer methacrylates (Buck et al. 2011).
- Fluorotelomer sulfonic acids (FTSA): The n:2 fluorotelomer sulfonic acids (n:2 FTSA) have been detected in environmental matrices at sites where aqueous film-forming foam (AFFF) has been used, and also in wastewater treatment plant effluents and landfill leachate. FTSA are precursor compounds and can undergo aerobic biotransformation to form PFCAs (Buck et al. 2011).
- Fluorotelomer carboxylic acids (FTCA): These compounds form through the biodegradation of FTOHs (Figure 2-8; (Buck et al. 2011; Liu and Mejia Avendaño 2013) and have been detected in landfill leachate. Note that the –COOH functional group on these fluorotelomer compounds means they may have either an even or odd number of carbons, so they may have n:2 or n:3 prefixes.

#### 2.2.4.2 Perfluoroalkane Sulfonamido Substances

The subgroups of perfluoroalkane sulfonamido substances shown in Figure 2-3 and discussed below have been detected in the environment and humans (Buck et al. 2011). Perfluoroalkane refers to the fully fluorinated carbon chain tail, but these compounds also contain one or more CH<sub>2</sub> groups in the head of the molecule attached to the sulfonamido spacer (Figure 2-10). They are either used as raw materials for surfactant and surface treatment products, or they are present as intermediate transformation products of these raw materials. As shown in the degradation pathways in Figure 2-8, some perfluoroalkane sulfonamido substances have been found to degrade to PFOS (Mejia Avendaño and Liu 2015). Environmentally relevant perfluoroalkane sulfonamido substances include:

- N-Alkyl perfluoroalkane sulfonamides (N-alkyl FASAs) are raw materials/intermediate environmental transformation products that include N-methyl perfluorooctane sulfonamide (MeFOSA) and N-ethyl perfluorooctane sulfonamide (nEtFOSA) (Buck et al. 2011).
- Perfluoroalkane sulfonamido ethanols (FASEs) and N-alkyl perfluoroalkane sulfonamido ethanols (MeFASEs, EtFASEs, BuFASEs) are raw materials for surfactant and surface treatment products (Buck et al. 2011). Figure 2-10 illustrates the structure of nEtFOSE
- Perfluoroalkane sulfonamido acetic acids (FASAAs) and N-alkyl perfluoroalkane sulfonamido acetic acids (MeFASAAs, EtFASAAs, BuFASAAs) are intermediate transformation products of FASEs, MeFASEs, EtFASEs, and BuFASEs (Figure 2-8) (Buck et al. 2011).

**Figure 2-10. Example of a perfluoroalkane sulfonamido ethanol (FASE).**

#### 2.2.4.3 Other Polyfluoroalkyl Substances

Other polyfluoroalkyl substances shown in Figure 2-3 include:

- polyfluoroalkyl ether sulfonic acids (PFESAs)
- polyfluoroalkyl ether carboxylic acids
- other fluorotelomer (FT)-based substances.

As discussed in Section 2.4.6, some PFAS have been developed or used as replacements for other PFAS that are phased out of use and production.

One replacement compound for the use of PFOA as a polymerization aid in the production of PTFE is a polyfluoroether carboxylate surfactant: ammonium 4,8-dioxa-3H-perfluorononanoate ( $\text{CF}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCH}_2\text{CF}_2\text{COO}^-\text{NH}_4^+$  (CAS No. 958445-44-8), commonly referred to by the trade name ADONA (Gordon 2011). The chemical structure is shown in Figure 2-11.

**Figure 2-11. Chemical structure for ADONA.**

Other replacement polymerization compounds for the manufacture of PTFE and polyvinylidene fluoride (PVDF) include cyclic or polymeric functionalized perfluoropolyethers (PFPEs) (Wang, Cousins, et al. 2013). A sample chemical structure is shown in Figure 2-12.

**Figure 2-12. Sample chemical structure for a non-polymer functionalized PFPE.**

## 2.2.5 Chemical Manufacturing

To differentiate among PFAS in understanding a conceptual site model for environmental risk assessment, it is important to know about the chemical manufacturing processes. The various manufacturing processes produce different types of PFAS, such as linear and branched isomers (as discussed in this section), which may affect the environmental fate, treatment, toxicology, and site forensics for these chemicals. The type of PFAS that might be formed by the transformation of precursor PFAS at or related to an environmental release site also may depend on the manufacturing process (refer to the family tree in Figure 2-3).

### 2.2.5.1 Processes

Two major processes, electrochemical fluorination (ECF) and fluorotelomerization, have been (and are) used to manufacture PFAS substances that contain perfluoroalkyl chains: side-chain fluorinated polymers, perfluoroalkyl acids and polyfluoroalkyl surfactants (USEPA 2003b; Benskin, DeSilva, and Martin 2010; KEMI 2015b; OECD 2018). The fluorotelomerization process may also be characterized as “oligomerization,” as it involves using tetrafluoroethylene (TFE) monomer and adding one to nine TFE monomers to form a perfluoroalkyl chain (Kissa 2001; Rao and Baker 1994). ECF and fluorotelomerization can be used to create some of the same PFAS, as shown on Figure 2-3. PFASs are produced only using the ECF process, whereas PFCAs can be produced by both ECF and fluorotelomerization (USEPA 2003b; CONCAWE 2016 )

More than 600 intermediate processes have been used to further produce certain PFAS and the associated final products. Further discussion of the intermediate processes may be found in the general scientific literature and numerous textbooks specifically written about fluorinated organics and fluoropolymers (Banks, Smart, and Tatlow 1994).

### Electrochemical Fluorination (ECF)

The Simons ECF process was licensed by 3M in 1945; 3M subsequently built an ECF pilot in 1949 and started commercial production in 1951 (3M Company 1999a) In the ECF process, an electric current is passed through a solution of an organic feedstock and liquid anhydrous

hydrogen fluoride, which causes the hydrogen atoms to be replaced by fluorine atoms, thereby creating carbon-fluorine bonds (3M Company 1999a; USEPA 2003b; Buck et al. 2011). ECF is used to create perfluoroalkane sulfonyl fluorides (PASFs), which are the building blocks for other sulfonyl-based PFAS, as well as perfluoroalkyl carboxylate derivatives. These ECF-synthesized PFAS can contain a variable mixture of linear and branched perfluorinated isomers, as well as other homologues, byproducts, and impurities (USEPA 2003b; Buck et al. 2011). The variable composition is caused by the process conditions, raw materials, and equipment used by the ECF process (3M Company 1999a; CONCAWE 2016). Subsequent processes (for example, hydrolysis, base neutralization) are then used to refine the compounds (USEPA 2003b).

Historically, the ECF process was primarily used to produce POSF-based compounds. This includes PFOS, which is often a terminal degradation product of POSF-based compounds. ECF was also used to produce perfluorooctanyl derivatives (for example, using perfluorooctane carbonyl fluoride to produce PFOA and its salts, such as APFO). As part of the phaseout of production of select long-chain PFAS in the United States, 3M has ceased using ECF to make certain long-chain PFAS, such as POSF-based compounds (PFOS and PFHxS) and PFOA (Buck et al. 2011) (Section 2.4.1). 3M's phaseout did not include other, shorter chain PASF-based products, such as those based on PBSF (3M Company 2018).

### **Fluorotelomerization**

Fluorotelomerization involves the reaction of perfluoroethyl iodide (PFEI,  $\text{CF}_3\text{CF}_2\text{-I}$ ) with tetrafluoroethylene (TFE,  $\text{CF}_2=\text{CF}_2$ ) to yield a mixture of even-numbered carbon linear perfluoroalkyl iodides ( $\text{C}_n\text{F}_{2n+1}\text{-I}$ ,  $n = 4, 6, 8, 10$ , etc.), commonly known as "Telomer A." Telomer A is then reacted with ethylene to make "Telomer B" (perfluoroalkylethyl iodides (PFEIs),  $\text{C}_n\text{F}_{2n+1}\text{CH}_2\text{CH}_2\text{-I}$ ,  $n = 4, 6, 8, 10$ , etc.). Telomer B is reacted to make fluorotelomer alcohols (FTOHs,  $\text{C}_n\text{F}_{2n+1}\text{CH}_2\text{CH}_2\text{-OH}$ ,  $n = 4, 6, 8, 10$ , etc.) Telomer A, Telomer B, and FTOHs are the basic raw materials used to manufacture fluorotelomer-based surfactant (nonpolymer) and polymer products (Kissa 2001; Rao and Baker 1994).

As part of the USEPA 2010/2015 Stewardship Program (USEPA 2018a; Section 2.4.3), eight major global fluorotelomer manufacturers phased out production of long-chain (Table 2-2) fluorotelomer-based products that were potential precursors to PFOA and other long-chain perfluorocarboxylic acids (PFCAs). Today, the major global fluorotelomer manufacturers are reported to have refined their processes and predominantly manufacture short-chain ( $\text{C}_6$ ) fluorotelomer-based products (<https://www.americanchemistry.com/ATCS/>). Some manufacturers outside of the United States (for example, China, India) have not phased out long-chain PFAS production (Song et al. 2018).

Fluorotelomerization has been primarily used to produce linear (straight-chain) PFAS isomers with an even number of carbon atoms (Buck et al. 2011), although some sources indicate that the process can also produce compounds with an odd number of carbons and branched chains (Lindstrom, Strynar, and Libelo 2011; Danish EPA 2015).

### **2.2.5.2 Linear and Branched Isomers of PFAS**

Many PFAS may be present as mixtures of linear and branched isomers (Figure 2-13) depending on the manufacturing process that was used. These structural differences are important because

they may affect how the compounds behave in the environment and may provide an indicator of their source. Structural differences are described below:

- A linear isomer is composed of carbon atoms bonded to only one or two carbons, which form a straight carbon backbone. There can be only one linear isomer in a C<sub>n</sub> homologue (compounds with the same number of carbons in their tail) series.
- In a branched isomer, at least one carbon atom is bonded to more than two carbon atoms, which forms a branching of the carbon backbone. There can be many isomers per C<sub>n</sub> homologue series.

### **Figure 2-13. Linear and one branched isomer of PFOS.**

For simplicity, both linear and branched isomers are abbreviated using the same acronym in this document. Note that other nomenclature conventions further identify PFAS by labeling linear isomers (for example, n-PFOS) and branched isomers based on the location of the branch in the carbon chain (for example, 5m-PFOS) (Benskin, DeSilva, and Martin 2010).

The formula “C<sub>n</sub>F<sub>2n+1</sub>” (where n is greater than or equal to 3) includes linear and branched structures. For example, PFOS and PFH<sub>x</sub>S are routinely present in environmental samples as a mixture of linear and branched isomers (Beesoon et al. 2011) (Beesoon et al. 2012) (Benskin, DeSilva, and Martin 2010).

Accurate quantification of PFAS that are mixtures of linear isomers and branched isomers in environmental matrices can be difficult (Riddell et al. 2009). However, the relative contributions of isomers may be useful in understanding sources of PFAS and the age of the source, because the production of isomers varies by manufacturing processes. For example, as discussed above, the fluorotelomerization process has been primarily used to produce mostly linear PFAAs, whereas the ECF process produces a mixture of linear and branched PFAA isomers (Table 2-3). Refer to Section 10.3 for more information on PFAS source identification. The presence of linear and branched isomers may also have implications for partitioning, transport, and bioaccumulation (Section 10.5).

### **Table 2-3. Manufacturing processes and potential PFAAs produced**

## **2.3 Emerging Health and Environmental Concerns**

Like other emerging contaminants, knowledge and concern about PFAS in the environment has evolved through a series of phases discussed in this section:

- discovery and/or synthesis of PFAS, followed by growth in commercial production and use (Section 2.2.5)
- emerging health and environmental concerns, including:
  - awareness of potential health impacts (Section 2.3.1)
  - analytical developments (Section 2.3.2)
  - detection in the environment (Section 2.3.3)
  - response in science, regulatory, and legal actions (Section 2.3.4)

- subsequent efforts to reduce use of contaminants of concern and/or replace the contaminants of concern with alternate technologies and chemicals, accompanied by health and environmental questions about those chemicals (Section 2.4)

### 2.3.1 Awareness of Potential Health Impacts

Occupational studies in the 1970s found detections of some PFAS in the blood of exposed workers, and further studies in the 1990s reported detections in the blood of the general human population (Buck et al. 2011). In recent years, the presence of several long-chain PFAAs (PFOA, PFOS, PFNA, and PFHxS) have been measured in the low parts per billion (ppb, equivalent to nanograms per milliliter (ng/ml)) range in the blood serum of almost all residents of the United States and other industrialized nations (Kato 2015; CDC 2018). These PFAS are present whether or not people were exposed in the workplace, likely due to the widespread use of PFAS in consumer products and industries (Kannan et al. 2004; Kärman et al. 2006; Olsen et al. 2003). Further information and discussion of studies and human health effects can be found in Section 7.1.

These findings led to increased awareness of PFAAs in the environment, associated human exposure, and the potential for health effects. Occupational workers may be more highly exposed, and at risk, than other populations (ATSDR 2018b). Laboratory studies using animals and epidemiological studies of human populations show that exposure to some PFAS may be associated with a wide range of adverse human health effects (USEPA 2016c; USEPA 2016d; ATSDR 2018e). Toxicity studies have mostly focused on PFOS and PFOA, as well as some other long-chain PFAAs (Section 7.1). More recently, the toxicology of other PFAS, such as fluorotelomers and shorter chain PFAAs, as well as replacement PFAS chemicals (such as GenX chemicals, Section 2.4.6), have received increased attention (CONCAWE 2016; USEPA 2016c; USEPA 2018g).

ATSDR is undertaking a national, multi-site PFAS health study to study how PFAS-impacted drinking water may harm health (ATSDR 2020b). The study was authorized by the National Defense Authorization Acts of 2018 and 2019. According to ATSDR, “The information learned from the multi-site study will help all communities in the U.S. with PFAS exposures, including those that were not part of the study.” The multi-site health study builds on the Pease Health Study at former Pease Air Force Base in Newington, NH, which effectively serves as a pilot program. The health study is intended to provide a better understanding of the cause and effect relationship between PFAS at various concentration and specific health outcomes based on adults and children. The study is expected to improve upon epidemiological studies with limited information about exposure factors.

### 2.3.2 Analytical Developments

Early detection of PFAS in environmental media was hindered by the analytical capability challenges arising from the unique surface-active properties of PFAS (Giesy and Kannan 2001; 3M Company 2000b). Since the 2000s, methods have been, and continue to be, developed with lower detection limits (for example, parts per trillion (ppt)) in water. <External Review 1 change> More commercial laboratories now offer these analytical capabilities. Analytical methods continue to be developed and improved to test a variety of media and additional PFAS

765 that continues to improve our knowledge of PFAS in the environment and potential human  
766 health effects. For further information on analytical methods, refer to Section 11.

767 The list of PFAS that can be tested for has also evolved over time, with longer lists of  
768 compounds and changing commercial availability helping to drive the evolving health and  
769 environmental concerns. Early focus was on PFOA and PFOS, but nationwide testing of drinking  
770 water supplies under the USEPA's Third Unregulated Contaminant Monitoring Rule (UCMR3)

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led to four additional PFAAs (PFHpA, PFNA, PFBS, PFHxS) gaining greater attention. More information about UCMR3 is provided in Section 6.3, and a summary of the occurrence data for the six PFAAs analyzed during UCMR3 is provided in Section 8.2.2.2. In Germany, von der Trenck et al. (2018) presented health- and ecological-based PFAS significance thresholds for 7 of 13 priority PFAS for the assessment of contaminated groundwater.

Many state regulatory agencies now request or require testing for an expanded list of long- and short-chain PFAAs, and some potential precursors to PFAAs, such as fluorotelomers. Other polyfluoroalkyl substances are also receiving increased attention, as illustrated in Figure 2-14. Many of these PFAS are also summarized in Figure 2-4.

**Figure 2-14. Emerging awareness and emphasis on PFAS occurrence in the environment.**

<External Review 1 change> Since the early 2000s, three analytical methods have been developed, validated, and published by USEPA for the analysis of PFAS in drinking water. In order of development, these include Methods 537, 537.1, and 533 (USEPA 2020<sup>1</sup>). According to USEPA, these methods were developed for accuracy, precision, and robustness and have been through multi-lab validation and peer review. USEPA notes that Method 537 was used extensively during Unregulated Contaminant Monitoring Rule 3, described above. These methods were developed for finished drinking water from groundwater and surface water sources. Most recently (December 2019), USEPA published Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (USEPA 2019f). Method 533 includes additional PFAS analytes not included in Method 537.1, including shorter-chain PFAS and fluorotelomers. Methods 537.1 and 533 have both been validated for the analysis of HFPO-DA (a component of the GenX processing aid technology). For more information, refer to Section 11.2 – Analytical Methods/Techniques.

The PFAS analytes associated with Methods 537, 537.1, and 533 are listed in Table 2-X and categorized according to the family tree hierarchy. < Classifications to be cross checked internally within HUNC section and to Buck et al. 2011 >

**Table 2-X EPA PFAS Drinking Water Methods and PFAS Classifications**

<sup>1</sup> USEPA, April 27, 2020, EPA PFAS Drinking Water Laboratory Methods: <https://www.epa.gov/pfas/epa-pfas-drinking-water-laboratory-methods>

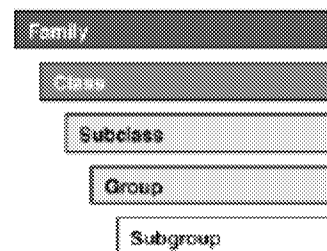


EPA PFAS Drinking Water Methods PFAS Classifications								
Analyte	Abbreviation	CASRN	EPA Method 537 (March 2020)	EPA Method 533 (Dec 2019)	Class	Subclass	Group	Subgroup
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (F-53B Minor)	11Cl-PF3OUdS	763051-92-9	X	X	Nonpolymer	Polyfluoroalkyl Substances	Chlorinated Functionalized PFPE	Chlorinated PFECA
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (F-53B Major)	9Cl-PF3ONS	756426-58-1	X	X	Nonpolymer	Polyfluoroalkyl Substances	Chlorinated Functionalized PFPE	Chlorinated PFECA
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	X	X	Nonpolymer	Polyfluoroalkyl Substances	Functionalized PFPEs	PFECA
Hexafluoropropylene oxide dimer acid (Gen-X)	HFPO-DA	13252-13-6	X	X	Nonpolymer	Perfluoroalkyl Substances	Functionalized PFPEs	PFECA
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6		X	Nonpolymer	Perfluoroalkyl Substances	Functionalized PFPEs	PFECA
Perfluorobutanoic acid	PFBA	375-22-4		X	Nonpolymer	Perfluoroalkyl Substances	PFAAs	PFCA
Perfluorobutanesulfonic acid	PFBS	375-73-5	X	X	Nonpolymer	Perfluoroalkyl Substances	PFAAs	PFSA
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4		X	Nonpolymer	Polyfluoroalkyl Substances	Fluorotelomer-based Substances	FTSA
Perfluorodecanoic acid	PFDA	335-76-2	X	X	Nonpolymer	Perfluoroalkyl Substances	PFAAs	PFCA
Perfluorododecanoic acid	PFDoA	307-55-1	X	X	Nonpolymer	Perfluoroalkyl Substances	PFAAs	PFCA
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7		X	Nonpolymer	Perfluoroalkyl Substances	Functionalized PFPEs	PFESA
Perfluoroheptanesulfonic acid	PFHpS	375-92-8		X	Nonpolymer	Perfluoroalkyl Substances	PFAAs	PFSA
Perfluoroheptanoic acid	PFHpA	375-85-9	X	X	Nonpolymer	Perfluoroalkyl Substances	PFAAs	PFCA

EPA PFAS Drinking Water Methods PFAS Classifications								
Analyte	Abbreviation	CASRN	EPA Method 537 (March 2020)	EPA Method 533 (Dec 2019)	Class	Subclass	Group	Subgroup
<u>1H,1H, 2H, 2H-Perfluorohexane sulfonic acid</u>	<u>4:2FTS</u>	<u>757124-72-4</u>		<u>X</u>	<u>Nonpolymer</u>	<u>Polyfluoroalkyl Substances</u>	<u>Fluorotelomer-based Substances</u>	<u>FTSA</u>
<u>Perfluorohexanesulfonic acid</u>	<u>PFHxS</u>	<u>355-46-4</u>	<u>X</u>	<u>X</u>	<u>Nonpolymer</u>	<u>Perfluoroalkyl Substances</u>	<u>PFAAs</u>	<u>PFSA</u>
<u>Perfluorohexanoic acid</u>	<u>PFHxA</u>	<u>307-24-4</u>	<u>X</u>	<u>X</u>	<u>Nonpolymer</u>	<u>Perfluoroalkyl Substances</u>	<u>PFAAs</u>	<u>PFCA</u>
<u>Perfluoro-3-methoxypropanoic acid</u>	<u>PFMPA</u>	<u>377-73-1</u>		<u>X</u>	<u>Nonpolymer</u>	<u>Perfluoroalkyl Substances</u>	<u>Functionalized PFPEs</u>	<u>PFECA</u>
<u>Perfluoro-4-methoxybutanoic acid</u>	<u>PFMBA</u>	<u>863090-89-5</u>		<u>X</u>	<u>Nonpolymer</u>	<u>Perfluoroalkyl Substances</u>	<u>Functionalized PFPEs</u>	<u>PFECA</u>
<u>Perfluorononanoic acid</u>	<u>PFNA</u>	<u>375-95-1</u>	<u>X</u>	<u>X</u>	<u>Nonpolymer</u>	<u>Perfluoroalkyl Substances</u>	<u>PFAAs</u>	<u>PFCA</u>
<u>1H,1H, 2H, 2H-Perfluorooctane sulfonic acid</u>	<u>6:2FTS</u>	<u>27619-97-2</u>		<u>X</u>	<u>Nonpolymer</u>	<u>Polyfluoroalkyl Substances</u>	<u>Fluorotelomer-based Substances</u>	<u>FTSA</u>
<u>Perfluorooctanesulfonic acid</u>	<u>PFOS</u>	<u>1763-23-1</u>	<u>X</u>	<u>X</u>	<u>Nonpolymer</u>	<u>Perfluoroalkyl Substances</u>	<u>PFAAs</u>	<u>PFSA</u>
<u>Perfluorooctanoic acid</u>	<u>PFOA</u>	<u>335-67-1</u>	<u>X</u>	<u>X</u>	<u>Nonpolymer</u>	<u>Perfluoroalkyl Substances</u>	<u>PFAAs</u>	<u>PFCA</u>
<u>Perfluoropentanoic acid</u>	<u>PFPeA</u>	<u>2706-90-3</u>		<u>X</u>	<u>Nonpolymer</u>	<u>Perfluoroalkyl Substances</u>	<u>PFAAs</u>	<u>PFCA</u>
<u>Perfluoropentanesulfonic acid</u>	<u>PFPeS</u>	<u>2706-91-4</u>		<u>X</u>	<u>Nonpolymer</u>	<u>Perfluoroalkyl Substances</u>	<u>PFAAs</u>	<u>PFSA</u>
<u>Perfluoroundecanoic acid</u>	<u>PFUnA</u>	<u>2058-94-8</u>	<u>X</u>	<u>X</u>	<u>Nonpolymer</u>	<u>Perfluoroalkyl Substances</u>	<u>PFAAs</u>	<u>PFCA</u>
<u>N-ethyl perfluorooctanesulfonamidoacetic acid</u>	<u>NEtFOSAA</u>	<u>2991-50-6</u>	<u>X</u>		<u>Nonpolymer</u>	<u>Polyfluoroalkyl Substances</u>	<u>Perfluoroalkane sulfonamide substances</u>	<u>EtFASAA</u>

EPA PFAS Drinking Water Methods PFAS Classifications								
Analyte	Abbreviation	CASRN	EPA Method 537 (March 2020)	EPA Method 533 (Dec 2019)	Class	Subclass	Group	Subgroup
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9	X		Nonpolymer	Polyfluoroalkyl Substances	Perfluoroalkane sulfonamide substances	MeFASAA
Perfluorotetradecanoic acid	PFTA	376-06-7	X		Nonpolymer	Perfluoroalkyl Substances	PFAAs	PFCA
Perfluorotridecanoic acid	PFTTrDA	72629-94-8	X		Nonpolymer	Perfluoroalkyl Substances	PFAAs	PFCA

## Family Hierarchy Legend



### 2.3.3 Detection in the Environment

Although some PFAS have been manufactured since the 1950s, PFAS were not widely documented in environmental samples until the early 2000s, as PFAS testing was not widely available until that time. Since the early 2000s, however, the occurrence of PFAS in the environment has been a very active area of research. The occurrence of certain PFAS has been reported in a wide variety of matrices, including sediments, surface and groundwater, and wildlife (Kannan et al. 2004; Yamashita et al. 2005; Higgins et al. 2005; Rankin et al. 2016). As noted above, UCMR3 sampling detected PFAS in 4% of drinking water supplies across the country, including in 33 states, three territories, and one Native American community (Hu et al. 2016). Initially, investigations focused mainly on major releases from manufacturing sources and significant PFAS uses such as firefighting foam application sites.

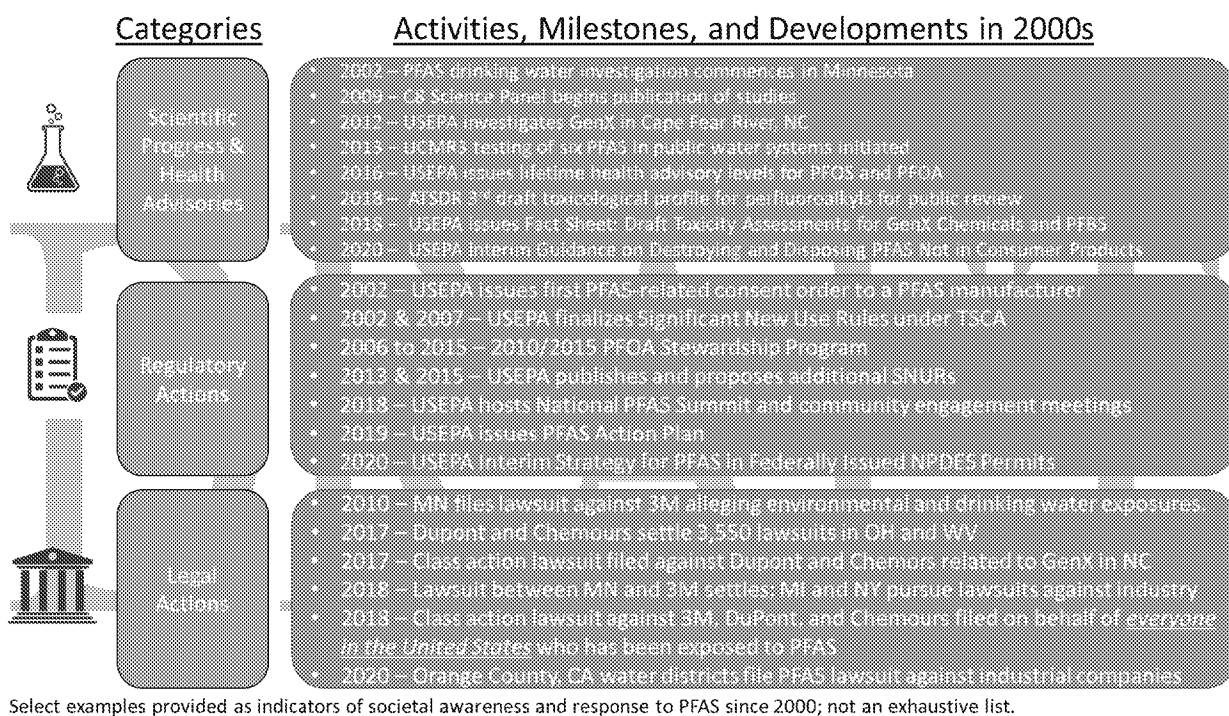
802 In recent years, with more sensitive analytical methods available, studies have detected PFAS (especially PFAAs) in locations throughout the  
803 globe, even in areas well beyond where they

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were initially used or manufactured (Houde et al. 2011). Detections of certain PFAS in the environment in various media are detailed in Section 6, and ecological effects are described in Section 7.2.

### 2.3.4 Growing Awareness and Concern

Societal awareness and concern about PFAS have increased since regulatory activity began in the early 2000s. Societal awareness and response are documented in the form of scientific progress and health advisories, federal regulatory actions, and legal actions. Major milestones of these are summarized in Figure 2-15. Other milestones, such as the growth of knowledge and investigation at major manufacturing and DOD sites in various U.S. states, are not discussed here.



**Figure 2-15. Growing awareness and concern since the early 2000s.**

## 2.4 PFAS Reductions and Alternative PFAS Formulations

Concern regarding the persistence, bioaccumulation, and possible ecological and human health effects of long-chain PFAAs has led manufacturers to use replacement PFAS chemistries, which include reformulating or substituting longer chain substances with generally shorter chain perfluoroalkyl or polyfluorinated substances that should not degrade to long-chain PFAAs, or replacing manufacturing processes with nonfluorinated chemicals or alternate methods (USEPA 2006a; OECD 2017). Manufacturing reductions and phaseouts are described in this section.

### 2.4.1 3M Voluntary Phaseout of Certain Long-Chain PFAS

In early 2000, 3M was the principal worldwide manufacturer of PFOA and POSF-derived PFAS (for example, PFOS) (Buck et al. 2011). This represented about 80–90% of global POSF-based

production (Prevedouros et al. 2006), with 3M the sole U.S. manufacturer of PFOS (USEPA 2003b). In 2000, 3M announced a voluntary, unilateral phaseout (this only applied to 3M) of POSF-derived PFAS, which at the time represented more than 95% of the company's perfluorooctanyl production (3M Company 2000a). The 3M phaseout included the six-, eight-, and ten-carbon PFASs (PFHxS, PFOS, and PFDS) and related precursors, as well as PFOA (Buck et al., 2011). 3M reportedly completed most of the phaseout by the end of 2002, with the remaining phaseout completed by 2008 (USEPA 2017e); (3M Company 2017).

At the time of the phaseout, 3M's POSF-derived PFAS were used in several applications:

- ~41% for paper and packaging protectors
- ~36% for textiles, leather, and carpet treatment and fabric protectors
- ~19% as industrial surfactants, additives, and coatings (including electroplating and etching surfactants, household additives, insecticides, and other applications)
- ~3% in firefighting foam (3M Company 2000a).

The paper and packaging protectors included POSF-based side-chain fluorinated polymers and phosphate diesters (Wang, Cousins, et al. 2013).

PFOA produced by 3M was primarily used as a fluoropolymer processing aid, with only about 3% of PFOA production used for other applications: mostly in antistatic coatings in medical films, with limited quantities used for electronics applications (for example, to create a humidity barrier on printed circuit boards and to coat precision bearings with silicone oil) (3M Company 2003).

This phaseout applied only to 3M, and only to select PFAS. 3M subsequently used (and reportedly continues to use) ECF to produce PBSF-based PFAS (for example, the four carbon PFSA: PFBS) (OECD 2013), (Wang, Cousins, et al. 2015)). Any new manufacture and/or import of the PFAS phased out by 3M requires USEPA review based on the Significant New Use Rules (SNURs) described in Section 2.4.2. Based on the 2012 Chemical Data Reporting effort, no company reported manufacture or import of PFOS into the United States (reporting was required for quantities greater than 25,000 pounds) (USEPA 2018a).

When 3M stopped producing PFOA in the early 2000s, it is reported that the manufacture of PFOA was continued by other domestic producers using fluorotelomerization (USEPA 2003b). Domestic PFOA production was later phased out by the eight major domestic producers as described in Section 2.4.3.

## 2.4.2 USEPA Significant New Use Rules (SNURs)

In conjunction with these voluntary reductions and phase-outs, USEPA used its authority under the Toxic Substances Control Act (TSCA) to finalize four SNURs between 2002 and 2013 to require notification to USEPA before any manufacture (including import) of select PFAS, which include, but are not limited to, some of the PFAS included in 3M's voluntary phaseout of PFOS and related chemicals (Section 2.4.1). USEPA proposed another SNUR for select PFAS in 2015 that has yet to be finalized, primarily focused on certain PFCAs (e.g., PFOA) and their precursors included in the 2010/2015 PFOA Stewardship Program (Section 2.4.3). For further discussion of the SNURs, including 2020 developments, see Section 8.

### 2.4.3 USEPA PFOA Stewardship Program

In January 2006, USEPA initiated the 2010/2015 PFOA Stewardship Program (USEPA 2006b). Most PFOA produced in 2003 (around the time of the phaseout described in Section 2.4.1) was used as a processing aid in the manufacture of fluoropolymers, such as PTFE (USEPA 2003b), and this was likely still the case at the time the stewardship program began.

The eight major manufacturing or processing companies that participated in the program are reportedly those that manufactured or processed the majority of these chemicals, including Arkema, Asahi, BASF Corporation (successor to Ciba), Clariant, Daikin, 3M/Dyneon, DuPont, and Solvay Solexis (USEPA 2018a). There may be other manufacturing or processing companies that did not participate in the program (USEPA 2015d). USEPA indicated that the eight participating companies successfully met the program goals, meeting a 95% reduction by 2010 in global facility emissions and product content, and eliminating production (100% reduction) of PFOA, certain longer chain PFCAs (higher homologues such as PFNA and PFDA), and related PFOA precursors (for example, 8:2 FTOH) by 2015 (USEPA 2017e). Even though the program goals were met by the eight companies, the ongoing use of PFOA stock and imported materials has not been fully restricted (USEPA 2018a). Products manufactured and imported prior to 2015, and materials with ongoing uses, may still contain these PFAS (USEPA 2018b), and PFOA may be present as a trace contaminant in some other PFAS and fluoropolymer products (3M Company 2003). As discussed in Section 2.4.5, production is ongoing in other nations.

### 2.4.4 Stockholm Convention on Persistent Organic Pollutants

The Stockholm Convention on Persistent Organic Pollutants (POPs) is a United Nations treaty signed in 2001 aimed at reducing or eliminating the production, use, and release of key POPs. POPs are defined as synthetic, organic compounds that, to varying degrees, resist photolytic, biological, and chemical degradation (KEMI 2004, 2015b); (USEPA 2017j). Chemicals listed as POPs satisfy screening criteria for persistence, bioaccumulation, long-range environmental transport, and adverse effects (Stockholm Convention 2001). The Stockholm Convention targets PFAS in these ways:

- In 2009, Annex B of the Stockholm Convention (which restricts production and use) was amended to include PFOS (and its salts and POSF), because it is persistent in the environment and is not known to degrade at any environmental condition. Currently, the United States has not ratified the amendment (KEMI 2017)). Annex B is not an outright ban; it allows certain approved uses and exemptions of POPs. Prior to 2019, approved, ongoing uses for PFOS under Annex B included select applications in photoimaging, semiconductor coatings and etching agents, metal plating, insect baits, chemically driven oil production, aviation hydraulic fluids, some medical devices, and color printer electronic parts (UNEP 2008, 2009).
- According to the Stockholm Convention website:
  - In May 2019, Annex B was amended to discontinue several of the previously allowed ongoing uses (UNEP 2019a).
  - Annex A was amended in May 2019 to prohibit and/or eliminate the production and use of PFOA (its salts and PFOA-related compounds), with certain exemptions (UNEP 2019a).

- the POPs Review Committee recommended in October 2019 to list PFHxS (and its salts and related compounds) in Annex A without specific exemptions (UNEP 2019b)

#### 2.4.5 Global Manufacture and Use of PFAS

PFAS are still manufactured globally, despite some PFAS (most notably PFOA and PFOS) no longer being produced in the United States, Europe, and Japan (FluoroCouncil 2018). For further information, see OECD's "Risk Reduction Approaches for PFASs" (OECD 2015b). In addition to the domestic reductions discussed in Section 2.4.1 and 2.4.3, some of the phase-outs and restrictions are summarized below.

In 2017, the South Australia state government took initial steps to develop legislation banning environmentally harmful foams, such as Class B firefighting foams containing PFAS (SA EPA 2017).

Canada embarked on an Environmental Performance Agreement with four major manufacturers to phase out PFOA and related compounds from 2010 to 2015 (CEPA 2006). In 2008, Canada prohibited the use of most PFOS, with select exemptions such as use of existing stocks of PFOS-based firefighting foams, and then added PFOS to the Virtual Elimination List in 2009 and to the Prohibition of Certain Toxic Substances Regulations in 2016 (CEPA 2018). By 2016, Canada prohibited the import, manufacture, use and sale of PFOS, PFOA, and other long-chain PFCAs (and salts and precursors), with limited exemptions (CEPA 2018), and subsequently in 2018, Canada proposed further modification to those restrictions (Government of Canada 2018).

In 2009, the European Union (EU), through the European Chemicals Agency (ECHA), regulated PFOS as a POP, and use of PFOS is limited to certain restrictions (Vierke et al. 2012). In 2017, the EU banned the sale, use, and import of PFOA, its salts and PFOA-related substances through Annex XVII of the European Chemicals Regulation (REACH), with phase-outs occurring through 2032 and certain allowed uses. ECHA is currently considering restrictions for other long-chain PFCAs, their salts and precursors, as well as other compounds, such as PFHxA (ECHA 2018).

In Japan, there are restrictions on the manufacture, import, export, and use of PFOS and its salts (OECD 2015a).

The global reduction anticipated with the U.S. phaseout of PFOA has potentially been offset by increased production of PFOA and related PFAS in China, India, and Russia (OECD 2015b). PFAS manufacture began in China in the 1980s (World Bank 2017b) (2017a), and PFOS production in China increased coincident with the long-chain PFAA phaseout in the United States (CONCAWE 2016) (OECD 2015b). In 2016, PFOS and its derivatives were still being produced in Germany, Italy, and China (TTE 2016), but by early 2017, China was the only known producer of PFOS. China has ratified the Stockholm Convention on POPs and was awarded a grant from the Global Environment Facility (GEF) in 2017 to support the reduction of PFOS in China (World Bank 2017b). China has developed some guidance for restriction and limitations of some PFAS (OECD 2015b). In Brazil, EtFOSA, which is a precursor to FOSA and PFOS and used in the pesticide sulfluramid, which is still being produced on an industrial scale, is allowed as an approved use by the Stockholm Convention (Löfstedt Gilljam et al. 2016).



There does not appear to be a comprehensive reference publically available to document the individual PFAS and the quantity of PFAS produced over the years. This is possibly because these data are proprietary, but also due to modifications to chemistries and products over the years (Lindstrom, Strynar, and Libelo 2011), complexity of the issue, and the general lack of publically available data (OECD 2018). That said, some estimates of production and emissions of select PFAS have been made based on the limited available data.

Prevedouros et al. (2006) estimated global emission of PFCAs at about 3,500–8,000 tons between the 1950s and 2002, with approximately 80% of emissions related to fluoropolymer manufacture (and use), based on overall annual production estimates of:

- APFO (ammonium salt of PFOA)-about 335–525 tons per year between 1951 and 2002
- APFN (ammonium salt of PFNA)-about 60–225 tons per year between 1975 and 2004
- POSF (building block for PFOS)-about 9,550 tons per year from 1960 to 2002.

Other production and emissions estimates for PFCAs are available from OECD (2015b), and for PFOS and PFOS precursors from Armitage et al. (2009), and Paul, Jones, and Sweetman (2009). OECD (2015b) calls for a new, comprehensive survey to evaluate both historical and ongoing emissions.

#### **2.4.6 PFAS-Based Replacement Chemistry**

With the emerging awareness of potential health and environmental impacts of some PFAS and related limitations on production of some PFAS, such as the SNURs (Section 2.4.2) and 2010/2015 PFOA Stewardship Program (Section 2.4.3), manufacturers began efforts to replace the use of long-chain PFAS chemistries with nonfluorinated chemicals, alternate technologies, and/or other, shorter chain PFAS (Wang, Cousins, et al. 2013). For example, decorative chrome plating typically now uses less toxic chromium III instead of chromium VI so that PFAS are not needed (Wang, Cousins, et al. 2013).

Some of the replacement chemicals are said to achieve the same performance effectiveness of some of their predecessors. A carpet manufacturer has found that performance of fluorine-free alternatives is “equivalent or superior to the fluorinated treatments” pg. 66, (CalEPA 2018). Conversely, a 2015 study concluded that there are no nonfluorinated alternatives that provide equivalent technical performance in textiles (Danish EPA 2015). PFAS-free AFFF has yet to be demonstrated to meet US Department of Defense performance specifications, but have been adopted by some other users (Section 3.8.1 and 3.10).

Several studies suggest some of the alternate PFAS chemistries may or may not be less hazardous than the long-chain predecessors, although publicly available information on most replacement chemicals is limited (Wang, Cousins, et al. 2015) (RIVM 2016); (OECD 2015b). Documentation regarding the USEPA’s review of hundreds of “shorter chain-length PFAS telomeric” substitutes is available under the TSCA New Chemicals Program (OECD 2013); (USEPA 2017i), and other documentation regarding replacement PFAS chemistries is available from the FluoroCouncil (2017). Draft toxicological evaluations have been provided for public comment by the USEPA for GenX chemicals and PFBS (USEPA 2018d) (USEPA 2018e). For further discussion of toxicity documentation for select PFAAs and replacement chemistries, see Section 7.

Although a full discussion of such PFAS chemistries is not possible here, it is important to be aware of the trend toward shorter chain chemistries, as some of these PFAS increasingly may be detected in the environment. Some replacement PFAS have been detected in the environment and generated public concern and regulatory actions; however, information on significant environmental contamination by replacement PFAS is limited, and most are not detected by standard analytical methods (Wang, Cousins, et al. 2013). Some PFAS used as replacement chemicals, such as HFPO-DA and ADONA (used as replacements for APFO/PFOA in PTFE manufacture), and F53B (used as a replacement for PFOS in plating), have recently been added to USEPA Method 537.1 (Shoemaker and Tetttenhorst 2018). Treatment processes used to remove these chemicals from waste streams may not be as effective as with longer chain PFAS (Sun et al. 2016).

Alternate PFAS chemistries are being used to replace long-chain PFAAs that have been phased out of production and/or use. In many cases, although similar legacy PFAAs were manufactured and used by many companies, these same companies have transitioned to the use of many different types of other PFAS as alternative chemicals. Many of these replacement PFAS are structurally similar to their long-chain predecessors, and are typically also manufactured using electrochemical fluorination (ECF) or fluorotelomerization (Wang, Cousins, et al. 2015) (CONCAWE 2016). Some of these fluorinated substitutes may degrade to form short-chain PFAAs. Some short-chain PFAAs, PFECAs, and related chemicals were manufactured as early as the 1980s, or earlier (Wang, Cousins, et al. 2015). Some PFAS used to replace long-chain PFAS are presented below (Hori et al. 2006; OECD 2007; Herzke, Olsson, and Posner 2012; Buck 2015; Wang, Cousins, et al. 2013; Wang et al. 2014; Wang, Cousins, et al. 2015; KEMI 2015b; Sun et al. 2016; Holmquist et al. 2016):

- short chain homologues of the long-chain PFAAs, including PBSF-based derivatives (for example, 4-carbon chain PFBS in lieu of POSF-based six-, eight-, and ten-carbon chain compounds) in many applications, including surface treatment
- perfluorohexane sulfonyl fluoride (PFHxSF, which can degrade to PFHxS and is considered to be phased out in the United States) as an alternative to PFOS, primarily in China
- fluorotelomer-based products such as FTOH, for example, those with a six-carbon perfluorohexyl chain, including 6:2 fluorotelomer-based compounds in AFFF formulations and other six-carbon fluorotelomer-based products, side-chain fluorinated polymers, and PFPE products for surface treatment of food contact materials
- per- and poly-fluoroalkyl ether substances used as polymerization aids in manufacture of fluoropolymers, such as GenX chemicals (Section 2.2.3.5) and ADONA used as a replacement for APFO in the manufacture of PTFE, as well as other types of PFAS, such as cyclic or polymeric functionalized PFPEs as a replacement for APFN in the manufacture of polyvinylidene fluoride (PVDF)
- 6:2 fluorotelomer-based compounds, a PFBS-based compound, and fluorotelomer-based F-53 and F-53B (perfluoroalkyl ether potassium sulfonate) in lieu of PFOS in metal plating applications.

## 2.5 PFAS Uses

PFAS have been produced on a commercial scale since the 1950s, and production continues today. The unique physical and chemical properties of PFAS impart oil, water, stain, and soil

repellency, chemical and temperature resistance, friction reduction, and surfactant properties to a wide range of products, some of which are considered essential to health, safety, or modern life (Gluge, J. et al., 2020).

Gluge, J., et al. (2020) categorize PFAS use according to industry application and practical use, including:

- use – the area in which the substances are employed
- function – the task that the substances fulfil in the use
- properties – why PFAS are able to fulfil this function

Gluge, J. et al., (2020) identify more than 200 uses of PFAS in 64 use categories for more than 1400 individual PFAS, including newly identified PFAS uses, such use in ammunition, climbing ropes, guitar strings, artificial turf, and soil remediation.

Table 2-4 provides a general (not exhaustive) introduction to some of the uses of PFAS fluorochemistries that are, or have been, marketed or used (3M Company 1999a)) (Poulsen 2005) (OECD 2006) (Washington State Department of Ecology 2012) (OECD 2011) (OECD 2013) (Fujii, Harada, and Koizumi 2013) (OECD 2015b) (FluoroCouncil 2018) (Henry et al. 2018). The specific applications for all PFAS are not well documented in the public realm. For example, of the 2,000 PFAS identified in a 2015 study, only about half had an associated listed use (KEMI 2015b). Further discussion of select uses that may be associated with potentially significant environmental releases are provided in Section 2.6.

As discussed in Section 2.2.2.1, most polymer PFAS are considered to pose relatively less risk to human health and the environment than some nonpolymer PFAS. For this reason, Table 2-4 distinguishes between these two major classes of PFAS and where they are used in various industries and products. Gluge, J., et al. (2020) provide a detailed listing of PFAS by use category/subcategory, function, and properties; however, it is not organized according to polymer versus non-polymer PFAS used in these instances.

The major industries and applications summarized in the table are described in more detail in Section 2.6.1.

#### **Table 2-4. Sample historic and current uses of PFAS**

### **2.6 PFAS Releases to the Environment**

This section summarizes sources of PFAS releases to the environment that have the potential for significant environmental impact, based on the type and magnitude of the release, and the types and concentrations of PFAS associated with that release. These sources are sites where PFAS could be, or are known to have been, released to the environment, even if the site is not the location where the PFAS were generated or used. Refer to Section 2.1 for a discussion of the relative significance of releases and source control, as not all of these facilities will have, or have been documented to have, PFAS releases, and not all releases are of the same magnitude.

These major sources are located both in the United States and abroad, and include:

- 1070 • industrial facilities that produce PFAS or process PFAS, or facilities that use PFAS  
1071 chemicals or products in manufacturing or other activities (Section 2.6.1)
- 1072 • areas where fluorine-containing Class B firefighting foams are stored, used, or released  
1073 (Section 2.6.2)
- 1074 • waste management facilities, such as landfills (Section 2.6.3)
- 1075 • wastewater treatment residuals and areas of biosolids production and application, with  
1076 more significant impacts associated with industrial wastewater discharges (Section 2.6.4).

1077 The fate and transport processes and distribution of PFAS in the environment are discussed in  
1078 Section 5. Media-specific occurrence data are discussed in Section 6. Information about risk  
1079 assessment, and human and ecological receptors is included in Section 9. Discussion of  
1080 conceptual site model (CSM) components for each of the PFAS release categories listed above  
1081 is included in Section 10.2.1.

## 1082 **2.6.1 Major Manufacturing and Industry Sources**

1083 Industrial source sites include primary and secondary manufacturing facilities. Primary  
1084 manufacturing facilities are those where PFAS-containing products are synthesized and made  
1085 into products or chemical feedstocks, or where PFAS are used as processing aids in  
1086 fluoropolymer production. PFAS processing aids are not intended to be in the final product, but  
1087 may be present at trace quantities (3M Company 2003) (Buck et al. 2011).

1088 Secondary manufacturing facilities may use fluoropolymers and PFAS-based materials produced  
1089 at primary manufacturing facilities as part of industrial processes, such as the application of  
1090 coatings to finished products. In some industrial settings, PFAS are used for worker safety  
1091 purposes, such as using PFOS-based materials to suppress harmful mists during electroplating  
1092 activities (Section 2.6.1.3).

1093 PFAS composition and release mechanisms will vary for each facility. The composition of PFAS  
1094 released from industrial facilities depends on the type of PFAS produced or used by the facility.

1095 The general PFAS release mechanisms and pathways at industrial facilities are illustrated in  
1096 CSM Figure 2-16 and include wastewater and stormwater discharges; on- and off-site disposal of  
1097 solid wastes; accidental releases such as leaks and spills; and stack and fugitive emissions. Stack  
1098 emissions may result in aerial deposition of PFAS to soil and surface water (with subsequent  
1099 leaching and infiltration to groundwater) related to the facility (Davis et al. 2007; Shin et al.  
1100 2011), as well as short- and long-range air transport of PFAS. Industrial facilities may also  
1101 contain areas where fire training or fire response using AFFF has occurred, AFFF storage areas,  
1102 and AFFF fire suppression systems inside buildings. Like many AFFF release sites, industrial  
1103 sites may also have releases of co-contaminants (solvents, petroleum products, etc.) that could  
1104 potentially influence fate and transport of PFAS.

### 1105 **Figure 2-16. CSM for industrial sites.**

1106 The following subsections provide further details regarding potential sources of PFAS releases to  
1107 the environment from PFAS use in manufacturing or industrial processes; these are not presented  
1108 in order of the potential for significance of a release.

**1109 2.6.1.1 Building and Construction**

1110 Similar to other products, the chemical attributes of PFAS have led to advancements in building  
1111 and construction materials. One particular application has been in composite wood and oriented  
1112 strand board (OSB). Over the last 50 years, wood-based materials have used numerous additives  
1113 for product strength and durability. A recent study performed on wood samples and OSB found  
1114 primarily short-chain PFCAs and PFOA at concentrations ranging from 1.38 to 13.9 micrograms  
1115 per kilogram ( $\mu\text{g/kg}$ ) for PFCAs (Bečanová et al. 2016). Furthermore, wood fiber insulation has  
1116 been shown to contain high amounts of PFHpA and other 5- to 8-carbon chain PFCAs  
1117 (Bečanová et al 2016). Many manufacturers use urea- or phenol-formaldehyde due to their  
1118 performance and low cost; however, the composition of the resins used by many manufacturers  
1119 is proprietary.

1120 Other materials, including certain types of building insulation (phenolic foam) have shown high  
1121 amounts of PFOS. Additionally, PFAS (predominantly C8–C20 gamma-omega-perfluorotelomer  
1122 thiols with acrylamide) have been used in the production of light weight concrete, concrete  
1123 sandwich panels, and lightweight concrete blocks (Bečanová et al. 2016; Posner et al. 2013). The  
1124 prevalence of these building materials in the construction of fire training areas, AFFF storage  
1125 facilities, and other areas potentially exposed to PFAS led to potential issues with demolition  
1126 waste. The porous nature of these materials (for example, concrete, brick) could lead to PFAS  
1127 adsorption/absorption, representing a potential source of PFAS when disposed in landfills or  
1128 recycling facilities (Australia Government DOD 2019).

1129 PFAS, including fluoropolymers such as PTFE, are used in the manufacture of architectural  
1130 fabrics, such as those used in the construction of roof domes, including large stadiums and  
1131 transportation facilities (FluoroCouncil 2018).

1132 PFOS-related chemicals have several uses in paint and varnishes. They can be used as wetting,  
1133 leveling, and dispersing agents, and have also been used to improve gloss and antistatic  
1134 properties. Additionally, they can be used as additives in dyestuff and ink. Furthermore, they can  
1135 be used as pigment grinding aids or as agents to combat pigment flotation problems (KEMI  
1136 2004) (RPA 2004). Fluorosurfactants are commonly used in coatings application for substrate  
1137 wetting, leveling, reduction of surface tension, oil repellency, and dirt pickup resistance (Danish  
1138 EPA 2015; Posner et al. 2013).

1139 Information received from different suppliers within the paint and varnish industry suggests that  
1140 fluorinated surfactants in general are much more expensive alternatives compared to other  
1141 surfactants. Therefore, fluorosurfactants are used only for special purposes in paint and  
1142 varnishes, where it is necessary to gain such a low surface tension that no other (nonfluorinated)  
1143 alternatives can achieve (Danish EPA 2015).

**1144 2.6.1.2 Cable and Wiring**

1145 In the 1950s the wire and cable industry began to use extruded grades of PTFE. This is a  
1146 suspension polymerization process, which does not require surfactants, unlike dispersion  
1147 polymerizations (for example, Teflon-coated pans). Melt extrusion is the process by which most  
1148 fluoropolymers are applied to wires. For instance, FEP, PFA, and PVDF are heated to 260°C and  
1149 then melt extruded over wire to continuous lengths. The equipment used for melt-processable

1150 fluoropolymers requires temperature sensitivity of 427°F. PTFE is processed via paste extrusion  
1151 for coating PTFE over wires due to its high melting point (ASTSWMO 2015) (Kotthoff et al.  
1152 2015) (Lau et al. 2007) (Lindstrom, Strynar, and Libelo 2011) (Oliaei et al. 2013) (Renner 2001)  
1153 (Trudel et al. 2008). For more information on the safe handling of fluoropolymer resins during  
1154 processing, see the Plastics Industry Association (2019) guidance document.

### 1155 2.6.1.3 Metal Finishing and Plating

1156 Electroplating is a process that uses electric current to apply a metal coating to the surface of an  
1157 object. Metallic ions in an acidic electrolyte solution are used in the electrochemical deposition  
1158 of metal coatings to the surface of the cathode (USEPA 1996a).

1159 PFAS, particularly PFOS, have been used as mist suppressants that are added to metal plating  
1160 and finishing baths to prevent air emissions of toxic metal fumes. Gluge et al. 2020 identified  
1161 PFAS use in chrome, nickel, copper, tin and zinc plating for lowering surface tension. In the  
1162 United States, amendments to the National Emissions Standards for Hazardous Air Pollutants  
1163 (NESHAP) under the Clean Air Act included a requirement to phase out the use of PFOS-based  
1164 fume suppressants (a fume suppressant that contains 1% or greater PFOS by weight) in  
1165 chromium electroplating by 2015 (USEPA 2012e). Some countries have phased out the use of  
1166 PFOS in some electroplating operations, adopting the use of other fluorotelomers (for example,  
1167 6:2 FTS) as a substitute in hard chrome plating operations (Danish EPA 2015), (KEMI 2015b) or  
1168 changing decorative chrome plating operations to employ the less toxic trivalent chromium.  
1169 PFAS known as F-53B (11-Chlorocicosafluoro-3-oxaundecane-1-sulfonic acid [F-53B Minor]  
1170 and 9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid [F-53B Major]) has been used as a metal  
1171 plating mist suppressant in China (Bao, Y., et al., 2019)<sup>1</sup>, though it is included in TSCA and is  
1172 not approved for import into the United States.

1173 Many different types of electroplating solutions can be used in plating activities, including hard  
1174 and decorative chrome plating; chromic acid anodizing; nickel, cadmium, or lead plating; metal  
1175 plating on plastics; and alkaline zinc plating. Chrome electroplating is the most significant  
1176 contributor as it relates to PFAS use. In this process, PFAS are used as surfactants to reduce the  
1177 surface tension of the electrolyte solution. Historically, PFOS was commonly used at a  
1178 concentration of 5–10% to limit the development of bubbles and the emission of hexavalent  
1179 chromium aerosols to workplace air, thereby reducing the potential hazard to workers posed by  
1180 hexavalent chromium (USEPA 2009b) (OSHA 2013) (Danish EPA 2015).

1181 Studies show use of PFAS in these settings can result in high concentration wastewater  
1182 discharges (USEPA 2009b) and air emissions. Once the electrolyte solution can no longer be  
1183 used, it may be treated to remove chromium and other metals, but PFOS and other PFAS may be  
1184 present in effluent and deposited in sewage sludge (Danish EPA 2015). Investigations in  
1185 Minnesota traced PFOS releases from one chrome plating operation to a wastewater treatment

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<sup>1</sup> Bao, y., Huang, J., Cagnetta, G., and Yu, G., 2019, Removal of F-53B as PFOS alternative in chrome plating wastewater by UV/Sulfite reduction, Water Resources Research, 163:114907. <https://pubmed.ncbi.nlm.nih.gov/31369921/>

plant (WWTP) where elevated levels of PFOS were detected in the biosolids, effluent water, and fish in the receiving surface water (ATSDR 2008). Air emissions from another Minnesota chrome plater were found to have accumulated on the roof of the facility and from there contaminated stormwater and snow melting from the roof, which in turn contaminated the groundwater, a nearby surface water system, and fish (MPCA 2016).

According to a study by the Michigan Department of Environment, Great Lakes, and Energy (EGLE, August 2020<sup>2</sup>), metal finishers that had a history of using fume suppressants were found to have PFOS in wastewater effluent, noting that 15 percent of metal finishers were discharging to WWTPs at concentrations greater than screening criteria (12 ppt), and 5 percent were discharging greater than 1,000 ppt PFOS. Of the metal finishers discharging PFOS above screening criteria, 89 percent used hexavalent and / or trivalent chromium in their current or past processes. Chrome platers were determined to be in compliance with the NESHAP and many replaced PFOS with a fume suppressant containing 6:2 FTS. Some chrome platers did not use PFOS-containing chemicals to control fumes and have not been found to be sources of PFOS to WWTPs. Nearly half of the chrome platers regulated under the NESHAP utilized mechanisms other than chemical fume suppression. It was concluded that current effluent containing PFOS, from facilities that have complied with NESHAP, originates from historical use of PFOS-containing fume suppressants.

#### **2.6.1.4 Industrial Surfactants and Fluoropolymer Production**

PFAS have been, and currently are, instrumental as surfactants in industrial and commercial production. It is noted that many specific surfactant uses of PFAS are not publicallypublicly available or published (KEMI 2015b). Most well documented is the historical use of PFOA as a processing aid in the manufacturing of PTFE, where APFO is used to help mix together the chemicals needed to combine units of tetrafluoroethylene (TFE) to make PTFE. Similarly, APFN, the ammonium salt of perfluorononanoic acid (PFNA), has also been used in the production of PVDF. PVDF polymers that are produced with the aid of APFN are sold in solid phase, with notable residual APFN concentrations (100–200 ppm) (Prevedouros et al. 2006).

Since the voluntary phaseout of PFOA and related PFAS chemistries, replacement chemistries such as ADONA and the GenX process chemicals are now used in the production of fluoropolymers.

The PFAAs used as polymerization aids may occur as impurities/residuals in some fluoropolymer products; however, it is documented that PTFE does not degrade to significant levels of PFAAs during incineration (Aleksandrov et al. 2019) and fluoropolymers of low concern are shown to be stable (Henry et al. 2018).

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<sup>2</sup> EGLE, August 2020, Michigan Industrial Pretreatment Program (IPP): Identified Industrial Sources of PFOS to Municipal Wastewater Treatment Systems, [https://www.michigan.gov/documents/egle/wrd-ipp-pfas-initiative-identified-sources\\_699494\\_7.pdf](https://www.michigan.gov/documents/egle/wrd-ipp-pfas-initiative-identified-sources_699494_7.pdf)

1220 PFAS are also used in the manufacturing of plastics and fluoropolymers, rubber, and  
1221 compression mold release coatings. These have applications in tubing, piping, drums, molds, and  
1222 resins (Poulsen 2005) (Prevedouros et al. 2006).

#### 1223 **2.6.1.5 Paper Products and Packaging**

1224 Since the 1960s, PFAS have been used as grease-proofing agents on food contact materials  
1225 (FCM) to prevent oil, grease, and moisture from foods from leaking through the packaging. This  
1226 includes coated paper and cardboard such as pizza boxes, microwavable popcorn bags,  
1227 parchment paper, fast food wrappers, paper cups, pet food bags, and other items (Rao and Baker  
1228 1994) (Hekster, Laane, and De Voogt 2003) (Poulsen 2005) (Trudel et al. 2008) (Buck et al.  
1229 2011).

1230 The U.S. Food and Drug Administration (FDA) currently approves more than 90 unique  
1231 monomer and polymer PFAS in FCMs (USFDA 2016). In January 2016, the FDA rescinded  
1232 approval for three families of long-chain PFAS used in FCMs, but these had been voluntarily  
1233 removed from the market in 2011. N-MeFOSE and NetFOSE were historically used to produce  
1234 surface coatings for textiles and paper products (Zaggia and Ameduri 2012). PFAS currently  
1235 used in FCM include polyfluorinated polyether-based polymers and shorter chain PFAAs (Wang,  
1236 Cousins, et al. 2015) (Schaider et al. 2017).

1237 The most common PFAS detected in U.S. fast food wrappers include PFCAs (for example,  
1238 PFOA and PFHxA), PFSAAs (for example, PFBS), and fluorotelomer sulfonates (for example, 6:2  
1239 FTS) (Schaider et al. 2017). Six of 20 FCM tested were found to contain detectable levels of  
1240 PFOA even though in 2011 U.S. manufacturers had voluntarily agreed to stop distributing FCM  
1241 that were manufactured using PFOA via an FDA initiative. The methodology was not sensitive  
1242 enough to detect if the PFASs were intentionally added to the packaging material or if they were  
1243 attributed to unintentional background levels (Schaider et al. 2017). Refer also to Section 2.4.3  
1244 on the USEPA 2010/2015 PFOA Stewardship Program, which discusses the phaseout of PFOA  
1245 and potential sources of PFOA that may remain in commercial and consumer products.

#### 1246 **2.6.1.6 Photolithography/Semiconductor Industry**

1247 The semiconductor industry historically has used PFOS for their surface-active properties in the  
1248 fabrication of imaging devices such as digital cameras, cell phones, printers, and scanners  
1249 (Poulsen 2005). Studies have shown semiconductor waste streams containing the PFAAs PFBS,  
1250 PFHxS, PFOS, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, and PFDoA (Lin, Panchangam,  
1251 and Lo 2009). Similarly, in photolithography processes, PFOS has been used predominantly in  
1252 applying top-layer antireflective coatings (TARCs), bottom antireflective coatings (BARCs), and  
1253 etchants. Smaller quantities of PFOS and longer-chain PFAS have been used in wet etchants,  
1254 film developers, cleaners, protective coatings, and color filters (SIA 2008), with ongoing uses  
1255 permitted (Section 2.4).

#### 1256 **2.6.1.7 Textiles, Leather, and Apparel (Including Carpet and Furniture)**

1257 Surface treatment of textiles, leather, carpet, and furniture upholstery with PFAS to make them  
1258 stain, oil, and water repellent occurs both before (that is, at the factory) and after consumer  
1259 acquisition for ongoing stain, oil, and water repellency (Prevedouros et al. 2006); (Ahrens



1260 2011); (Herzke, Olsson, and Posner 2012). Aftermarket PFAS-containing stain-repellent  
1261 products for carpets allow consumers to treat carpets and textiles at home (Renner 2001)  
1262 (Hekster, Laane, and De Voogt 2003). Losses to the environment can be related to dry cleaning  
1263 and laundering activities (Poulsen 2005) (3M Company 2000b).

1264 Home textiles, including furniture and carpeting, as well as aftermarket PFAS surface treatment  
1265 products, are also sources of long-chain perfluorinated chemical exposure (Guo et al. 2009).  
1266 Textile coating operations may use water-emulsion or powdered feedstocks that contain greater  
1267 proportions of PFCAs compared to PFASs (Lassen et al. 2015) (Gremmel, Frömel, and Knepper  
1268 2016). According to California EPA (CalEPA) CalEPA (2018), pg. 12, “The PFAS polymers  
1269 used in carpets, rugs, and other textiles can contain various amounts of mobile residual raw  
1270 materials, impurities, or degradation products, including PFAAs and other PFAA precursors such  
1271 as fluorotelomer alcohols (FTOHs) and perfluoroalkyl sulfonamide alcohols.” Releases to the  
1272 environment could occur from disposal of carpet cleaning wastewater (CalEPA 2018). Physical  
1273 degradation of some consumer products (such as PFAS-treated textiles and carpets, as well as  
1274 paper) may be a source of PFAS in house dust (Björklund, Thuresson, and de Wit 2009).

1275 It should be noted that many treated home textiles and carpets are now manufactured with  
1276 alternatives to long-chain PFAS; however, these products can have a long useful life, making it  
1277 possible that items previously treated with long-chain PFAS are still in use (Brooke 2004). A  
1278 2009 study of over 100 consumer products conducted by the USEPA and Arcadis indicated that  
1279 pretreated carpet, treated upholstery and textiles, as well as other floor treatments, are likely the  
1280 largest source of PFAS receptor exposure in American homes (Guo et al. 2009).

1281 Other studies have since shown nonpolymeric PFAS in leather samples and outdoor textiles to  
1282 impart water, oil and stain resistance; applications include protective clothing, outerwear,  
1283 footwear, umbrellas, tents, and sails (OECD 2013; Walters and Santillo 2006) (Kotthoff et al.  
1284 2015). Durable water repellent (DWR) is a fabric surface finish that creates a protective barrier.  
1285 It is typically added at the factory, but is also available to consumers for apparel maintenance  
1286 (Brooke 2004). The finishes/treatments are applied to materials in mills/tanneries and as  
1287 aftermarket applications by professionals or do-it-yourself consumers as aqueous dispersions. In  
1288 some aftermarket applications, they are applied as solutions in hydrocarbon-based or halogenated  
1289 solvents (OECD 2013).

#### 1290 **2.6.1.8 Other Potential Commercial or Domestic Sources of PFAS Releases to the** 1291 **Environment**

1292 There is the potential for everyday uses of PFAS to result in relatively smaller releases of PFAS  
1293 to the environment. Of note, these may include, but are not limited to leaching from materials to  
1294 media (for example, well construction and plumbing materials), discharges to on-site wastewater  
1295 disposal systems from use of household products and cosmetics, discharges from car washing  
1296 and waxing, and use of ski waxes (professional ski wax technicians may have significant  
1297 inhalation exposures to PFAS (Nilsson et al. 2013). Snowmelt and surface waters near ski areas  
1298 may have measurable PFAS impacts (Kwok et al. 2013).

#### 1299 **2.6.2 Class B Fluorine-Containing Firefighting Foams**

1300 Some Class B firefighting foams designed for extinguishing flammable liquid hydrocarbon fires  
1301 and vapor suppression may contain fluorine. These foams can be a major source of local PFAS  
1302 release to the environment, with the CSM included in Figure 2-17.

1303 **Figure 2-17. CSM for fire training areas.**

1304 Class B firefighting foams are commercial surfactant solutions that have been (and continue to  
1305 be) stored and used for fire suppression, fire training, and flammable vapor suppression at  
1306 military installations and civilian facilities and airports (Hu et al. 2016), as well as at petroleum  
1307 refineries and bulk storage facilities, and chemical manufacturing plants and storage facilities  
1308 (CONCAWE 2016). Additionally, local fire departments in communities have used and may  
1309 maintain quantities of firefighting foam in their inventories for use in training and emergency  
1310 response. Facilities that manufactured firefighting foams and landfills that received firefighting  
1311 waste are also potential sources. Refer to Section 3 for more detailed information about  
1312 firefighting foams.

1313 **2.6.3 Solid Waste Management Facilities**

1314 Environmental releases associated with the use of PFAS-containing products are primarily  
1315 related to management of solid waste (for example, disposal of used items in a municipal solid  
1316 waste (MSW) landfill or other legacy disposal areas). Other solid waste facilities, such as scrap  
1317 yards and metal salvage facilities, might also be a potential source of release to the environment.  
1318 Some PFAS are considered hazardous waste by some states (Section 8).

1319 Landfills can be sources of PFAS because they are the ultimate repositories for PFAS-  
1320 contaminated industrial waste, sewage sludge from wastewater treatment facilities, and waste  
1321 from site mitigation, as well as for PFAS-bearing consumer wastes, such as goods treated with  
1322 hydrophobic, stain-resistant coatings (Busch et al. 2010) (Eggen, Moeder, and Arukwe 2010).  
1323 But the type and concentration of PFAS vary greatly among landfills, due to variations in the  
1324 waste streams. Industrial waste can be a significant source of PFAS in landfills (as well as in  
1325 wastewater and biosolids), particularly those that accept waste from facilities involved in the  
1326 production or application of PFAS (Oliaei et al. 2013). Although MSW will contain PFAS due to  
1327 its presence in so many consumer products, it generally is expected to have lower concentrations  
1328 than landfills that accept industrial waste. Given the production timeline of PFAS, industrial,  
1329 commercial, and consumer products and waste disposed since the 1950s are potential sources of  
1330 PFAS release to the environment. As PFAS manufacturing processes change with time, the  
1331 resulting type and composition of waste streams also change. PFAS production and use began  
1332 several decades before the enactment of federal and state regulations governing waste disposal;  
1333 as a consequence, environmental and drinking water impacts from disposal of legacy PFAS  
1334 industrial and consumer waste have been documented (Oliaei, Kriens, and Weber 2010) (Shin et  
1335 al. 2011) (MPCA 2017).

1336 **Figure 2-18 illustrates common elements of CSMs associated with the potential release**  
1337 **scenarios at waste management facilities.**

1338 **Figure 2-18. CSM for landfills and WWTPs.**

1339 **2.6.3.1 Landfill Construction**

Landfills are either lined or unlined (Figure 2-18). MSW landfills constructed since the 1990s are required by federal or state regulations to install a composite liner, a layer of compacted soil, and a leachate collection system (40 CFR 258.40). Although some states may have implemented construction standards at an earlier date, most landfills constructed before the 1990s were not required to have synthetic flexible membrane liners, compacted soil liners, or leachate collection systems, causing waste to be in direct contact with underlying soil or groundwater. Construction and demolition (C&D) landfills or nonmunicipal solid waste landfills are subject to the requirements specified in 40 CFR 257 Part A (and if they intend to accept very small quantity generator waste, they are also subject to 40 CFR 257 Part B). Minimum design criteria for landfill liners are not specified in 40 CFR 257. Therefore, new C&D and nonmunicipal solid waste landfills may be permitted and constructed (or new cells added to existing facilities) without synthetic liners. Some states may have more restrictive requirements. Therefore, unlined landfills (and legacy disposal areas not classified as landfills) have a higher potential of contributing PFAS to groundwater (Oliaei et al. 2013). Properly constructed and operated modern landfills provide one of the few available disposal/management options for PFAS-containing waste, including wastewater solids, remedial/treatment waste, and consumer products.

Landfills are currently required to use a daily cover or alternate daily cover. It is acceptable for alternative daily cover to include materials such as sludge, sludge-derived products, shredded automotive parts, spray-on foams, and other materials (Pohland 1993) that are possible sources of PFAS. Landfill caps reduce infiltration of water to waste and may reduce the overall mass of PFAS entering the environment from a landfill, but more research on their effectiveness is needed (Hamid, Li, and Grace 2018).

Leachate from some MSW landfills has been shown to be a source of PFAS release to the environment (Busch et al. 2010) (Eggen, Moeder, and Arukwe 2010), although the fate and transport processes for PFAS through landfills into leachate are not well understood at this time. The processes for managing leachate have implications on the ultimate fate and transport of PFAS. Leachate collected from landfills is typically treated on site or transported to either a WWTP or evaporation ponds. If liners or leachate collection systems fail, PFAS may directly enter the environment. Modern landfills with properly constructed and operated liner and leachate collection systems should generally protect the underlying groundwater from PFAS releases. Leachate treatment by WWTPs is common prior to discharge to surface water or distribution for agricultural or commercial use (Lang 2016)). However, standard WWTP technologies are generally ineffective at reducing or eliminating PFAS (Hamid and Li 2016), (Ahrens, Hedlund, et al. 2016) (CRC CARE 2017b). As a result, the discharge of landfill leachate, even if treated at WWTPs, can be a significant source of release of some PFAS to the environment (Ahrens et al. 2015) (CRC Care 2017).

### 2.6.3.2 Waste Age

Landfills containing sources of PFAS may continue to release PFAS to leachate at slow but relatively steady rates for decades following initial placement. In modeled anaerobic landfill reactors, most of the release is attributed to biological, not physical, mechanisms, indicating that the low solubility of the compounds is not solely responsible for slow release rates from landfills (Allred et al. 2015) (Lang et al. 2016). Although landfill leachate PFAS concentrations can be relatively high, landfill leachate discharged to WWTPs for treatment generally is considered a relatively minor source to the environment because the volume of leachate generated annually

and sent to a WWTP for treatment is low compared to the flow volume in most WWTPs (Busch et al. 2010). However, legacy industrial waste landfills may constitute a major source of PFAS release to the environment (ATSDR 2008) (2012).

### 2.6.3.3 PFAS Composition

PFAS composition and concentration in leachates vary depending on waste age, climate, and waste composition (Allred et al. 2015) (Lang et al. 2017). Relative concentrations of PFAS in leachate and groundwater from landfills are different from those at WWTPs and AFFF-contaminated sites. PFAS with fewer than eight carbons tend to dominate landfill leachate because they are less hydrophobic and therefore more likely to partition to the aqueous phase (Huset et al. 2011) (Higgins and Luthy 2007). In particular, 5:3 fluorotelomer carboxylic acid (FTCA) is a common and often dominant constituent of PFAS found in landfills and is released from carpet in model anaerobic landfill reactors. This compound could prove to be an indicator of PFAS in the environment originating from landfills (Lang et al. 2017, 2016).

PFAS may also be released to the air from landfills, predominantly as fluorotelomer alcohols (FTOHs) and perfluorobutanoate (PFBA). In one study, total PFAS concentrations were 5–30 times greater at landfills than at background reference sites (Ahrens et al. 2011). PFAS release rates vary with time for a given waste mass, with climate (for example, rainfall) as the apparent driving factor for the variations (Lang et al. 2017; Benskin, Li, et al. 2012). Gas collection systems commonly employed at modern landfills should reduce possible PFAS emissions to air.

## 2.6.4 Wastewater Treatment and Wastewater Treatment Residuals and Biosolids

Consumer and industrial use of PFAS-containing materials, including disposal of landfill leachate and firefighting foam, may discharge PFAS-containing wastewater to municipal and industrial WWTPs (Lin, Panchangam, and Lo 2009; Ahrens et al. 2009) private septic systems, or other wastewater disposal systems.

### 2.6.4.1 Wastewater Treatment

WWTPs can provide the following pathways for PFAS to the environment (Figure 2-18):

- point source discharges of effluent
- leakage or unintended releases from surface impoundments and structures
- air emissions
- management and disposal of biosolids and other byproducts generated during the treatment process (Section 2.6.4.2).

The composition of PFAS in these media is a function of the different sources to the WWTP influent and the WWTP processes (Chen, Lo, and Lee 2012; Oliaci, D. Kriens, and Kessler 2006; Frömel 2016) (Schultz et al. 2006), including:

- type and concentration of PFAS received by the WWTP, particularly those that receive industrial wastewater discharges from industrial facilities manufacturing or using PFAS
- biological and chemical transformation of polyfluorinated substances (that is, precursor PFAS) to intermediate and terminal degradation products, such as PFAAs

- physical or chemical partitioning, or both.

Conventional sewage treatment methods used in WWTPs do not efficiently remove PFAAs (Ahrens et al. 2011) (Schultz et al. 2006). Even WWTPs with advanced treatment technologies (such as granular activated carbon (GAC), powdered activated carbon (PAC), or reverse osmosis (RO)) may not fully remove all PFAS if these systems were not designed with the intent to remove PFAS in addition to other targeted contaminants. Some PFAAs are frequently detected in WWTP effluent (for example, PFOA and PFBS), with concentrations of some PFAS ranging up to hundreds of ng/L. Ahrens et al. (2011) and Hamid and Li (2016) suggested that WWTP effluent is a major source of PFAAs to surface waters.

Evaluation of full-scale WWTPs has indicated that conventional primary (sedimentation and clarification) and secondary (aerobic biodegradation of organic matter) treatment processes can change PFAS concentrations and subgroups. For example, studies have shown increased concentrations of PFAAs in effluent, presumably from degradation of precursor PFAS (Schultz et al. 2006), and the possible creation of PFAAs from the oxidation of polyfluorinated precursors during the treatment process (Oliaei, D. Kriens, and Kessler 2006) (Frömel 2016; Houtz 2018).

PFAS may be concentrated in wastewater solids (for example, sewage sludge) generated throughout the wastewater treatment process (Schultz et al. 2006). PFAS may also be present in septage (solids removed from septic systems). Depending on waste management and disposal practices, land application or landfill disposal of wastewater solids, biosolids, or septage could potentially contaminate the environment.

Hu et al. (2016) suggested that the presence of WWTPs in an area could be predictive of the presence of PFOS and PFOA in drinking water. PFOS and PFOA are two of the most frequently detected PFAS in wastewater (Hamid and Li 2016). Using WWTP effluent-impacted surface water as a source of drinking water can, in turn, recycle the PFAS back to the WWTP, recirculating PFAS in the water cycle (Hamid and Li 2016).

At some WWTPs, studies have shown concentrations of PFAS in ambient air at WWTPs to be 1.5–15 times greater than background reference sites (Hamid and Li 2016). Hamid and Li (2016) noted that these elevated air concentrations of total PFAS include polyfluoroalkyls and that this has important implications considering the potential for their long-range transport and subsequent degradation to recalcitrant PFAAs. PFAS distribution (primarily PFAAs and FTOH, with higher concentrations of FTOH) changes based on the specific PFAS sources in the effluent and the type of treatment methods employed at the WWTP. Lagoon systems contain a greater fraction of PFAAs.

#### **2.6.4.2 Biosolids Production and Application**

PFAS (measured as PFCAs and PFSAs) have been found in domestic sewage sludge (Higgins et al. 2005), and PFAS occurrence in biosolids is reported to be prevalent and nationwide (Venkatesan and Halsden 2013). Given that more than half of the sewage sludge produced in the United States is applied to agricultural land as biosolids (USEPA 2017m), there is the potential for release of PFAS to the environment associated with biosolids production and application. PFAS are not known to be added to biosolids during processing or application.

PFAS may be introduced to the environment through the land application of biosolids as a beneficial soil amendment, potentially allowing PFAS to enter surface water through runoff or to infiltrate to groundwater (Lindstrom et al. 2011). The potential effects on groundwater or surface water depend on the amount and composition of PFAS present in biosolids, soil properties, infiltration rate, and land application practices. PFAS concentrations can be elevated in surface and groundwater in the vicinity of agricultural fields that received PFAS-contaminated biosolids over an extended period of time (Washington et al. 2010). The Washington et al. study was completed in an area that received industrial wastewater discharges from several PFAS-related industrial dischargers. Other studies indicate that the potential PFAS releases from municipal biosolids (for example, those generated from facilities that do not receive PFAS-related industrial discharges), may still impact water quality, but at an apparent lower relative impact than at the industrial-influenced biosolids application sites (Gottschall et al. 2017).

The most abundant PFAS found in biosolids (PFOS and PFOA) are the same as those found in WWTP effluent, although biosolids may also contain other long-chain PFAS (Hamid and Li 2016). Although transformation polyfluorinated substances to PFAAs in land-applied biosolids has been suggested (Sepulvado et al. 2011), other evidence suggests that some polyfluorinated substances remain in biosolids-amended soils for many years (Rich et al. 2015).

Application of municipal biosolids as a soil amendment can result in a transfer of PFAS to soil (Sepulvado et al. 2011). These PFAS can then be available for uptake by some plants and soil organisms. There are indications that PFAAs can enter the food chain through the use of biosolids-amended soil (Lindstrom et al. 2011; Blaine et al. 2013; Blaine, Rich, Sedlacko, Hundal, et al. 2014) (Navarro et al. 2017). It is noted, however, that PFAAs present at one municipal biosolids application site were not found in grain grown in the application plot (Gottschall et al. 2017). Hamid and Li (2016) suggested that short-chain (< C7) PFAAs in biosolids subsequently used in land applications can lead to contamination of food (Section 5.6).

Message

**From:** Lesley Hay Wilson [lhay\_wilson@sagerisk.com]  
**Sent:** 2/23/2021 6:33:43 PM  
**To:** Richard, Ann [Richard.Ann@epa.gov]  
**Subject:** Re: ITRC PFAS Documents  
**Attachments:** PFAS\_Section2(11-18-20).docx

Ann —

The file, PFAS\_Section2(11-18-20) ar.pdf, I received only has a highlight on lines 95 - 96 the sentence about compounds with an aromatic component. Is this the correct file? I've attached the Word version of the file if you can paste your edits in there. We were also hoping that you could briefly expand the sentence about CompTox that appears at lines 98 and 99.

Thank you for your help,  
Lesley

\*\*\*\*\*

Lesley Hay Wilson, Ph.D.  
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phone: 512-327-0902

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The information contained in this electronic message and any attachments are intended for the exclusive use of the addressees and may contain confidential or privileged information. If you are not the intended recipient, please notify Lesley Hay Wilson immediately at (512) 327 - 0902 and destroy all copies of this message and any attachments.

**From:** "Richard, Ann" <Richard.Ann@epa.gov>  
**Date:** Monday, February 22, 2021 at 9:40 PM  
**To:** Lesley Hay Wilson <lhay\_wilson@sagerisk.com>  
**Cc:** "Sandra.Goodrow@dep.nj.gov" <Sandra.Goodrow@dep.nj.gov>, "Schlosser, KateEmma" <KateEmma.A.Schlosser@des.nh.gov>  
**Subject:** FW: ITRC PFAS Documents

Hi Leslie,

Please find attached some suggested edits to the first few sections of your terminology document. This is all I can offer for this week as I have to turn my attentions to an impending deadline for a presentation. I hope this is helpful, ,but feel free to further edit as needed.

Best regards,  
Ann

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Ann M Richard, PhD  
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## Section 2. Naming Conventions and Use

Review Note: This file contains new content for Sections 1 and 2 of the PFAS Guidance Document (PFAS-1):

- Revision in Section 1 - Introduction
- New text and figure for the main introduction to Section 2.
- Additions in Section 2.2 Chemistry, Terminology and Acronyms
- Additions in Section 2.2.2 Introduction to the PFAS Family
- Revisions in 2.2.3.5 Other Perfluoroalkyl Substances
- Revisions in 2.3.2 Analytical Developments

Please use the comments spreadsheet PFAS\_ExtRev1\_CommentSpreadsheet(11-18-2020).xlsx to provide your comments. Instructions are included in the spreadsheet. If additional context for the change is needed, please refer to the web version of the PFAS Technical and Regulatory Guidance Document, [ [HYPERLINK "https://pfas-1.itrcweb.org/"](https://pfas-1.itrcweb.org/) ].

### 1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a very large family of thousands of chemicals that vary widely in their chemical and physical properties, as well as their potential risks to human health and the environment. [ [C\\_nF\\_{2n+1}.](https://pfas-1.itrcweb.org/references/)

Fundamentally, PFAS are characterized by carbon atoms that are linked together with fluorine atoms attached to the carbons. Additional qualifying characteristics, such as a functional group, are described in [ [HYPERLINK "https://pfas-1.itrcweb.org/2-2-chemistry-terminology-and-acronyms/"](https://pfas-1.itrcweb.org/2-2-chemistry-terminology-and-acronyms/) ] along with evolving definitions of PFAS.

<Note: The text box on this page will be deleted. The Buck et al. (2011) quoted definition is included in Section 2.2, along with more detailed discussions.>

### 2. PFAS Chemistry and Naming Conventions, History and Use of PFAS, and Sources of PFAS Releases to the Environment

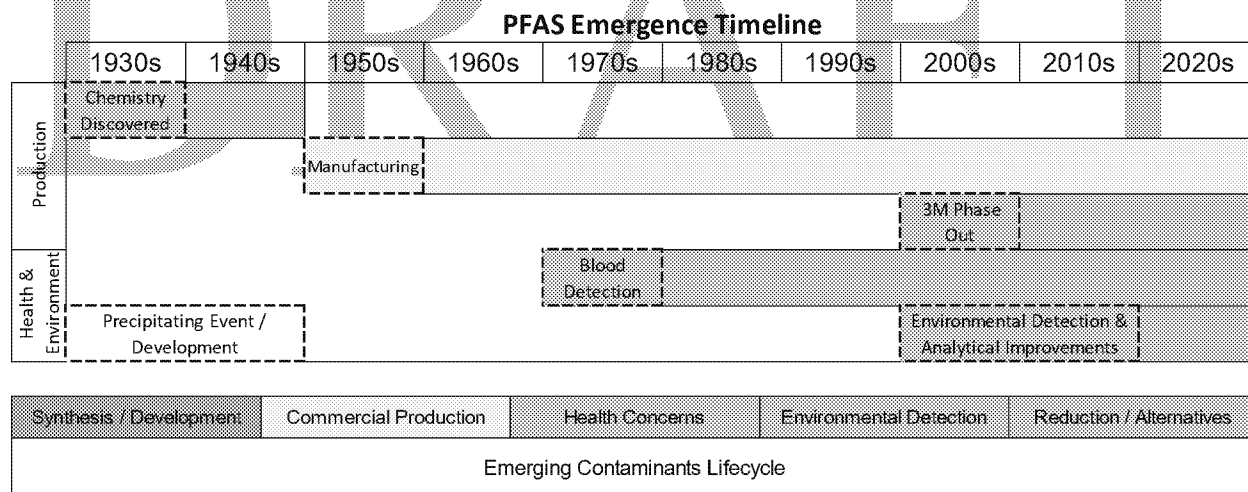
PFAS chemistry was discovered in the late 1930s. Since the 1950s, many products commonly used by consumers and industry have been manufactured with or from PFAS, as the unique physical and chemical properties of PFAS impart oil, water, stain, and soil repellency, chemical and thermal stability, and friction reduction to a range of products. These products have application in many industries, including the aerospace, semiconductor, medical, automotive, construction, electronics, and aviation industries, as well as in consumer products (such as

carpets, clothing, furniture, outdoor equipment, food packaging), and firefighting applications (3M Company 1999a; Buck et al. 2011; KEMI 2015a; USEPA 2017b).

The number of PFAS and their uses have expanded over the years. It has been estimated that the PFAS family may include approximately 5,000–10,000 chemicals (USEPA 2018i). A recent inventory of PFAS identified Chemical Abstracts Service (CAS) Registry Numbers found more than 4,700 PFAS that could have been, or may be, on the global market (OECD 2018), although the uses of each of these PFAS may not be known (KEMI 2015a). Publicly available health and toxicity studies are limited to only a small fraction of these PFAS, and modern commercially available analytical technologies typically identify only about 20–30 PFAS.

Scientific, regulatory, and public concerns have emerged about potential health and environmental impacts associated with chemical production, product manufacture and use, and disposal of PFAS-containing wastes. These concerns have led to efforts to reduce the use of or replace certain PFAS, such as the two most widely produced, commonly encountered, and most studied compounds: perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (USEPA 2016e; WA DER 2017).

PFAS have followed a similar pattern of emergence and awareness exhibited by many other anthropogenic environmental contaminants. Figure 2-1 provides a general timeline of PFAS emergence and awareness that includes categories of 1) Synthesis/Development, 2) Commercial Production, 3) Health Concerns, 4) Environmental Detection, and 5) Reduction / Alternatives.



**Figure 2-1. General timeline of PFAS emergence and awareness.**

*Graphic is intended to provide a general sense of PFAS emergence and awareness by decade with initial activity or precipitating event indicated for the start of each phase of emergence. It is not intended to be exhaustive or precise.*

*Source: J. Hale, Parsons. Used with permission.*

## 2.2 Chemistry, Terminology, and Acronyms

This section focuses on chemistry, terminology, names, and acronyms for those PFAS most commonly reported in the environment, identified in scientific literature, and those PFAS most commonly tested for by current analytical methods. Other important classes of PFAS are introduced. This section also introduces the chemical manufacturing processes that influence the types of PFAS that are found in the environment.

PFAS are characterized by carbon atoms that are linked together with fluorine atoms attached to the carbons. ~~A more specific and technical definition of PFAS states that PFAS are defined as~~ An early and widely recognized technical definition of PFAS is provided by Buck et al. (2011) who define PFAS as, “highly fluorinated aliphatic substances that contain one or more carbon (C) atoms on which all the hydrogen (H) substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by fluorine (F) atoms, in such a manner that they contain the perfluoroalkyl moiety  $C_nF_{2n+1}$  -.”

The definition of PFAS may evolve to reflect continued study of these compounds. For example, the definition of PFAS used in one study (OECD 2018) also included chemicals that contain –  $C_nF_{2n}$  – in addition to the  $C_nF_{2n+1}$  -, which includes chemicals with both ends of the carbon-fluorine chain connected to a functional group, such as cyclic analogs of linear PFAS.

~~More recently, the Michigan PFAS Action Response Team (MPART) offers a working description of polyfluoroalkyl substances, stating that the basic chemical structure is a chain (or tail) of two or more adjacent carbon atoms with a charged functional group head attached at one end. The functional groups commonly are carboxylate or sulfonate, but other forms are also detected in the environment. A linear or branched aliphatic tail structure can be written as:  $C_nF_{2n+1}-R$  where “ $C_nF_{2n+1}$ ” defines the length of the perfluoroalkyl chain tail, “n” is  $\geq 1$ , and “R” represents the attached functional group/head. The tail may be linear, or branched, or contain a cyclic portion, but it always contains adjacent fluorinated carbon atoms in a  $C_nF_{2n+1}$  moiety (with  $n \geq 2$ ). The functional group may contain one or more carbon atoms, which are included in the total number of carbons when naming the compound. [ HYPERLINK “https://pfas-1.itrcweb.org/2-2-chemistry-terminology-and-acronyms/” ] of this document describes polyfluoroalkyl substances.~~

An emerging subject of discussion is whether the presence of an aromatic component in a chemical’s structure still constitutes classification as PFAS.

For practical reference, the USEPA CompTox chemical dashboard provides useful information about PFAS ([https://comptox.epa.gov/dashboard/chemical\\_lists/PFASMASTER](https://comptox.epa.gov/dashboard/chemical_lists/PFASMASTER)).

## 2.2.2 Introduction to the PFAS Family

PFAS encompass a wide universe of substances with very different physical and chemical properties (Section 4), including gases (for example, perfluorobutane), liquids (for example, fluorotelomer alcohols), and solid material high-molecular-weight polymers (for example, PTFE). For this reason, it is helpful to group PFAS that share similar chemical and physical properties.

As shown in Figure 2-2, the PFAS family may be divided into two primary classes: polymers and nonpolymers. Each class may contain many subclasses, groups, and subgroups, some of which are shown in the figure. This document focuses primarily on those nonpolymer PFAS most commonly detected in the environment and those PFAS that may be significant as “precursors” that can transform to more persistent forms.

#### **Figure 2-2. The PFAS family.**

The family tree is further expanded in Figure 2-3, based on nomenclature provided in Buck et al (2011), Organization For Economic Co-operation and Development (OECD, 2015b), and Wang, DeWitt, et al (2017), with further introduction to some of these chemicals provided later in this section.

Future updates to the family tree and nomenclature are expected to be necessary given the evolving public knowledge of these compounds. For example, other PFAS without analytical standards are being identified using nontarget analyses by research laboratories ([ [HYPERLINK "https://pfas-1.itrcweb.org/11-sampling-and-analytical-methods/"](https://pfas-1.itrcweb.org/11-sampling-and-analytical-methods/) ]). These PFAS do not necessarily have an associated CAS number but are being identified by molecular structure.

Figure 2-3 is not inclusive of all PFAS and is intended to categorize a sampling of common PFAS chemistries. Additionally, as more information becomes available, there will be changes until that time. Figure 2-3 and is based on the information included in the references above.

An example of evolving classification includes whether perfluoropolyethers (PFPE) should be regulated as polymers or nonpolymers, since this chemical group can function (or be used) as either a polymer or a nonpolymer depending on the chemical structure (ionic character) and their intended use. These chemicals are often referred to as “functionalized PFPE.” It is recommended this chemical category be carefully evaluated and not assume that all of the PFPE chemistries will fall into either the polymer or nonpolymer classification.

Functionalized PFPE as a polymer, or Polymeric PFPE, can be used as a grease, solvent or lubricant. They are very large molecules (high molecular weight) and thereby tend to not be bioavailable and stable (not mobile) in the environment. They may have end groups that are significantly smaller, as compared to the length of the repeating units (backbone) and have little to no polar effect (not polarized). Section 2.2.2.1 includes more information about polymer PFAS.

Functionalized PFPE as a nonpolymer, can be used as a surfactant, soap or de-greaser. They are small (low molecular weight) making them more available for bioaccumulation and mobility in the environment. These chemistries have ionic end-groups (heads) which are used to capture or link together like-particles. Examples of Functionalized PFPE nonpolymers are ADONA (Section 2.2.4.3) and GenX (Section 2.2.3.5). Buck et al. (2011), pages 532-533, provides more information about PFPE.

#### **2.2.3.5 Other Perfluoroalkyl Substances**

Other perfluoroalkyl substances shown on Figure 2-3 include:

- perfluoroalkane sulfonyl fluorides [PASFs, such as perfluorooctane sulfonyl fluoride (POSF) and perfluorobutane
- sulfonyl fluoride (PBSF)], and perfluoroalkanoyl fluorides (PAFs), associated with the ECF process
- perfluoroalkyl iodides (PFAIs) and perfluoroalkane aldehydes (PFALs), associated with the fluorotelomerization process
- perfluoroalkyl ether carboxylic acids (PFECAs) and perfluoroalkyl ether sulfonic acids (PFESAs)

As discussed in Section 2.4, some PFECAs have been developed or used as replacements for other PFAS that are phased out of production and use. This includes GenX chemicals (see text box). Other emerging fluorinated replacement PFECAs more recently detected in the environment, such as perfluoro-2-methoxyacetic acid (PFMOAA), are described in Sun et al. (2016).

#### GenX Chemicals {TEXT BOX}

**Figure 2-7. Example replacement chemistry structure for GenX Ammonium Salt.**

In addition to linear and branched structures, certain cyclic structures have much in common with the non-cyclic PFAS and are consistent with the definitions and descriptions provided above. As an example, Figure 2-7 illustrates the structure of PFECHS (perfluoro-2-ethylcyclohexanesulfonate), which is a PFAS compound. It is used in airplane hydraulic fluids and has been found both in the environment (Labore et al. 2018; Howard and Muir 2010; De Silva et al. 2011; Lescord et al. 2018; Houdry et al. 2016) and in human blood (Miaz et al. 2020). It is a non-aromatic compound with a sulfonate active group connected to a perfluorinated two-carbon tail by a fully fluorinated six-carbon ring. PFECHS fits the Buck et al. (2011) description by having a fully fluorinated aliphatic tail of one or more carbon atoms attached to a charged functional group head.

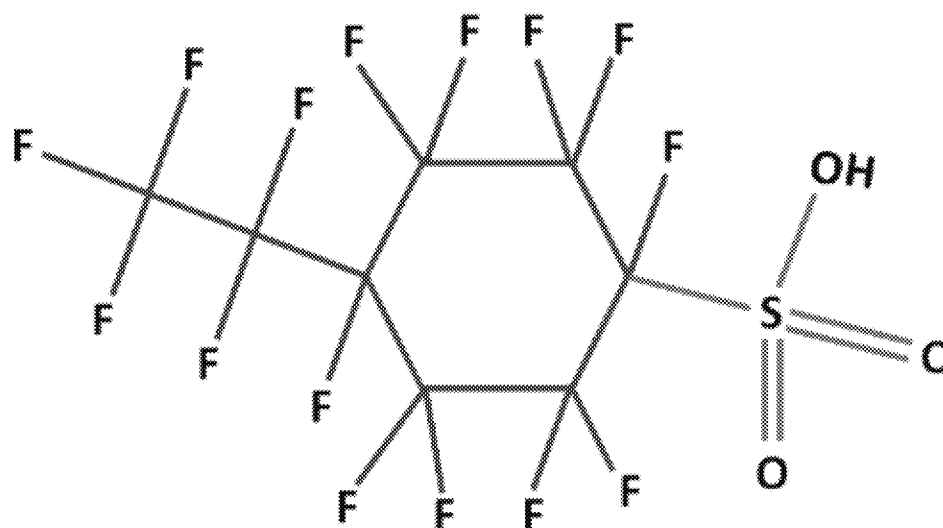


Figure 2 - # Illustration of perfluoro-4-ethylcyclohexanesulfonate (PFECyHS) Structure

Source: Michigan PFAS Action Response Team's Human Health Workgroup PFECyHS  
Whitepaper (May 15, 2020)

### 2.3.2 Analytical Developments

Early detection of PFAS in environmental media was hindered by the analytical capability challenges arising from the unique surface-active properties of PFAS (Giesy and Kannan 2001; 3M Company 2000b). Since the 2000s, methods have been, and continue to be, developed with lower detection limits (for example, parts per trillion (ppt)) in water, that are commensurate with levels of potential human health effects. More commercial laboratories now offer these analytical capabilities. Analytical methods continue to be developed and improved to test a variety of media and additional PFAS; these continue to improve our knowledge of PFAS in the environment and potential human health effects. For further information on analytical methods, refer to [ HYPERLINK "<https://pfas-1.itrcweb.org/11-sampling-and-analytical-methods/>" ].

The list of PFAS that can be tested for has also evolved over time, with longer lists of compounds and changing commercial availability helping to drive the evolving health and environmental concerns. Early focus was on PFOA and PFOS, but nationwide testing of drinking water supplies under the USEPA's Third Unregulated Contaminant Monitoring Rule (UCMR3) led to four additional PFAAs (PFHpA, PFNA, PFBS, PFHxS) gaining greater attention. More information about UCMR3 is provided in Section 6.3, and a summary of the occurrence data for the six PFAAs analyzed during UCMR3 is provided in Section 8.2.2.2. In Germany, von der Trenck et al. (2018) presented health- and ecological-based PFAS significance thresholds for 7 of 13 priority PFAS for the assessment of contaminated groundwater.

Many state regulatory agencies now request or require testing for an expanded list of long- and short-chain PFAAs, and some potential precursors to PFAAs, such as fluorotelomers. Other polyfluoroalkyl substances are also receiving increased attention, as illustrated in Figure 2-14. Many of these PFAS are also summarized in Figure 2-4.

**Figure 2-14. Emerging awareness and emphasis on PFAS occurrence in the environment.**

Since the early 2000s, three analytical methods have been developed, validated, and published by USEPA for the analysis of PFAS in drinking water. In order of development, these include Methods 537, 537.1, and 533 (USEPA 2020). According to USEPA, these methods were developed for accuracy, precision, and robustness and have been through multi-lab validation and peer review. USEPA notes that Method 537 was used extensively during UCMR 3, described above. These methods were developed for finished drinking water from groundwater and surface water sources. Most recently (December 2019), USEPA published Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (USEPA 2019f). Method 533 includes additional PFAS analytes not included in Method 537.1, including shorter-chain PFAS and fluorotelomers. Methods 537.1 and 533 have both been validated for the analysis of HFPO-DA (a component of the GenX processing aid technology). For more information, refer to Section 11.2 – Analytical Methods/Techniques.

DRAFT

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